JOURNAL

OF

THE CHEMICAL SOCIETY.

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1915. Vol. CVII. Part I., pp. 1–846.

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C.
1915.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BRUNSWICK ST., STAMFORD ST., S.E.,
AND BUNGAY, SUFFOLK.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Solutions of Bromine in Water, Nitrobenzene, and Carbon Tetrachloride.*

By Alfred Francis Joseph.

The colorimetric studies of bromine solutions previously communicated (T., 1911, **99**, 274; 1913, **103**, 1554) have dealt with the relations between the colour of polybromides and that of free bromine. The present paper records the fact that solutions of bromine in different solvents are of different colour intensities; whilst the different colour of iodine solutions has long been known, the similar but less obvious phenomenon in the case of bromine appears to have been overlooked.

Attempts have been made to correlate the colour with other physical properties. For the purpose of throwing light on the nature of the solutions, the most important are the solution volume, vapour pressure, viscosity, and solvent power, of which the first two are here dealt with.

The solvents used were water, nitrobenzene, and carbon tetrachloride, which were chosen on account of their widely different physical and chemical properties, and because bromine has practically no action on them in the cold.

I.—*Solution Volume of Bromine.*

The densities were determined in ordinary specific gravity bottles fitted with a well-ground cap over the neck. That they give

accurate results may be illustrated by the following five determinations of the water-content made at intervals of a few days: Bottle No. 10, water-content at 32·5° reduced to a vacuum:

(1)	49·72830
(2)	832
(3)	829
(4)	829
(5)	829

The fifth figure is of little significance, and need not be used in an actual density determination.

In using these bottles the only special precaution taken was to replace the stopper always in the same position relative to the neck. As an example of a duplicate density determination carried out with two bottles, that of carbon tetrachloride at 32·5° may be given, the results obtained being 1·56834 and 1·56835, which is good agreement for a somewhat difficult liquid. A large thermostat was used, fitted with a Lowry regulator and special arrangement for maintaining a constant gas pressure. The temperature was kept constant to 0·002°.

Materials.—The bromine and carbon tetrachloride were distilled over phosphoric oxide, the nitrobenzene was purified by freezing and two distillations, and freshly distilled conductivity water was used.

Method of Making the Solutions.

Water.—These were prepared by dissolving the approximately correct amount of bromine in water. After the density of the solution had been determined, it was transferred from the specific gravity bottle to a vessel of sulphurous acid, and the bromine determined gravimetrically by precipitation with silver nitrate.

Carbon Tetrachloride and Nitrobenzene.—These solutions lose bromine less easily than those in which water is the solvent, and were made up by directly weighing out the solvent and bromine.

In every determination with one of these solvents its density was determined as part of the experiment; by this means it is thought that slight errors, such as that which might be caused, for example, by the hygroscopic nature of nitrobenzene, were reduced to a minimum. The fresh samples of carbon tetrachloride had a density of 1·56834 at 32·5° and the nitrobenzene 1·19085.

Results.

Water.

Bromine by weight. Per cent.	Density at 32·5°.	Grams of bromine per litre.	Molecular solution volume.
0·7214	0·999814	7·212	50·94
1·1172	1·00252	11·201	51·21
1·6448	1·00610	16·548	51·82
1·9956	1·00887	20·133	50·54
2·5960	1·01320	26·303	50·07
	Nitrobenzene.		
1·5643	1·20225	18·807	52·92
3·2323	1·21449	39·166	53·06
4·6462	1·22518	56·924	53·24
6·1826	1·23603	73·573	53·03
	Carbon Tetrachloride.		
1·5449	1·58014	24·412	52·61
1·6454	1·58060	26·007	52·81
1·7990	1·58168	28·554	53·71
2·6676	1·58812	42·365	54·30
3·5833	1·59526	57·163	53·96

It will be seen that in each case the molecular solution volume passes through a maximum, but no deduction can at present be made from this. From the specific volume data of Thorpe (T., 1880, **37**, 173) the molecular volume of liquid bromine at 32·5° is 53·17, which is above the maximum solution volume in water and below that in nitrobenzene and carbon tetrachloride.

II.—*Colour of Bromine in the same Solvents.*

All the above solutions (with the exception of the most concentrated nitrobenzene solution) were examined in the colorimeter in the manner previously described, the non-volatile liquid used for comparison being 0·01 or 0·001 per cent. methyl-orange.*

A calibration curve was constructed showing the relation between cm. of methyl-orange standard and strength of bromine in carbon tetrachloride solution when contained in the colorimeter cell. The colour of the other solutions was measured by matching it against methyl-orange and then reading from the calibration curve the strengths of the carbon tetrachloride solution having the same colour. A solution of 1 gram of bromine in a litre of carbon tetrachloride solution is thus the standard, and its colour expressed as unity. All colour comparisons were made at the room temperature—approximately 28·5°.

* In the last communication (T., 1913, **103**), bottom of page 1555, it was stated that 0·1 per cent. methyl-orange was used. This should read 0·01 per cent.

Data for the Calibration Curve.

Concentration of bromine in carbon tetrachloride. Grams per litre	24·4	26·0	28·4	42·4	57·2
Cm. of 0·01 per cent. methyl-orange	1·62	2·00	2·22	4·80	9·10

Colour of Aqueous Solutions.

Concentration	7·2	11·2	16·5	20·1	26·0
Cm. standard	0·09	0·12	0·17	0·19	0·28
Concentration of bromine in carbon tetrachloride having the same colour	4·4	5·6	7·6	8·0	9·5

Colour of Nitrobenzene Solutions.

Concentration	18·8	24·1	39·2	56·9
Cm. standard	0·53	0·75	1·87	4·08
Concentration of bromine in carbon tetrachloride having the same colour	11·8	14·5	25·0	40·0

These results show clearly that the colour of bromine is greatest in carbon tetrachloride and least in water. By interpolation of the above tables, the colour of a 25 grams per litre solution can be estimated, and the figures compared with the maximum solution volumes in the same solvent.

	Water.	Nitrobenzene.	Carbon tetrachloride.
Maximum solution volume	50·8	53·2	54·3
Colour	9	13	25

The order is the same in the two cases.

An attempt was made to estimate the colour of bromine vapour in order to compare it with the foregoing. Two methods were used: in one, a 2 cm. cell was provided with a smaller cell (made from the bottom of a test-tube 1 cm. in diameter), which was filled with bromine. After the cell had been allowed to remain for an hour it was assumed that the space was saturated with bromine vapour, and the concentration of the bromine in the vapour space could consequently be calculated from the known vapour pressure of bromine at the temperature of the experiment. The colour was then matched against a methyl-orange standard, and from a calibration curve constructed for the cell used, the strength of a carbon tetrachloride solution of the same colour was read off. In a typical experiment the colour of the vapour at 28·8° was matched by 2·2 cm. of the standard. This is the colour of a carbon tetrachloride solution containing 2·2 grams of bromine per litre. Since at 28·8° the vapour pressure of bromine is 251 mm. (Ramsay and Young, T., 1886, **49**, 457), the space contains $\frac{160}{22{\cdot}4} \cdot \frac{251}{760} \cdot \frac{273}{302} =$ 2·1 grams of bromine per litre.

In the second method a little bromine was placed in the colorimeter cell and allowed to evaporate completely; the cell was then closed, and the colour of the vapour measured. It was then dropped into potassium iodide solution, and the liquid titrated with standard sodium arsenite.

As an example, the cell filled with vapour was found to have the same colour as when filled with a carbon tetrachloride solution containing 2·2 grams of bromine per litre. The cell (volume 13·9 c.c.) was then dropped into potassium iodide solution; the volume of 0·102*N*-sodium arsenite required was 3·65 c.c. This corresponds with 2·1 grams of bromine per litre.

These experiments indicate that the colour of bromine in carbon tetrachloride solution is the same as that of bromine vapour.

III.—*Relative Vapour Pressures of Bromine in Carbon Tetrachloride and Nitrobenzene.*

Water differs from these two solvents inasmuch as it is only partly miscible with bromine. The two others, however, mix freely with bromine at 28°, and the vapour pressure of the bromine should therefore indicate its relative affinity for the two solvents.* The comparison was effected by aspirating the same volume of air through solutions of bromine in the two solvents, interrupting the air current from time to time, and determining by analysis the amount of bromine evaporated.

The air was drawn by a filter-pump through ten Cloëz washing bottles arranged in the following order: (1) concentrated sulphuric acid to dry the air, (2) nitrobenzene to saturate it with that substance, (3) the nitrobenzene solution of bromine, (4) and (5) aqueous potassium iodide to absorb the bromine evaporated, (6) concentrated sulphuric acid, (7) carbon tetrachloride, (8) the carbon tetrachloride solution of bromine, (9) and (10) aqueous potassium iodide. The air then passed through a small gas-meter, which registered the volume aspirated. Bottles 2, 3, 7, and 8 were immersed in a thermostat at 29·2°. The air was passed at an approximately uniform rate of about 20 litres an hour. At suitable intervals the experiment was interrupted, and the contents of the potassium iodide bottles were titrated with standard sodium arsenite. At the end of the experiment the bromine remaining in bottles 3 and 8 was similarly estimated.

If a volume of air V be aspirated through a solution containing originally A grams of bromine per litre, and if x be the amount of

* For the relative vapour pressures of bromine in aqueous solution and aqueous salt solutions, see *Zeitsch. physikal. Chem.*, 1911, **76**, 156.

bromine evaporated, then $dx/dV = k(A - x)$, where k is the evaporation-coefficient: $k = 1/V \log A/A - x$.

The amounts of bromine are given in terms of c.c. of standard solution used, the actual initial concentration being given at the head of the tables.

Solution in Nitrobenzene containing 21·2 *Grams of Bromine per Litre.*

Total vol. of air. V litres.	dx.	$A-x$.	k (common logs.).
0	0	130·6	—
4·9	15·6	115·0	0·0112
9·4	12·5	102·5	0·0112
20·1	23·8	78·7	0·0109
29·2	16·3	62·4	0·0110
30·0	16·4	46·0	0·0113
52·2	13·6	32·4	0·0116
73·1	14·8	17·6	0·0119
			Mean 0·0113

Solution in Carbon Tetrachloride containing 21·4 *grams of Bromine per Litre.*

Total vol. of air. V (litres).	dx.	$A-x$.	k (common logs.).
0	0	131·8	—
4·9	29·2	102·6	0·0222
9·4	21·2	81·4	0·0222
20·1	33·9	47·5	0·0220
29·2	17·9	29·6	0·0222
40·0	13·1	16·5	0·0225
52·2	7·8	8·7	0·0226
73·1	5·8	2·9	0·0225
			Mean 0·0223

The evaporation-coefficient of bromine from solution in nitrobenzene is therefore only half of that from carbon tetrachloride.

In a similar way it has been found that bromine evaporates from water about twelve times as fast as from carbon tetrachloride, but the fact that water is only partly miscible with bromine prevents any comparison of it in this respect with the other two, owing to the intimate relationship which exists between aspiration-coefficient and solubility (compare Jones, T., 1911, **99**, 392).

Summary of Results.

(1) The solution volume of bromine in water, nitrobenzene, and carbon tetrachloride in concentrations up to 60 grams per litre increases to a maximum in each case. The value of the maximum is greatest for carbon tetrachloride, next for nitrobenzene, and least for water.

(2) The colour of carbon tetrachloride solution is practically the same as that of bromine vapour of the same concentration.

(3) The colour of nitrobenzene solution is about two-thirds that of carbon tetrachloride solutions.

(4) The colour of aqueous solutions is about a-half to one-third that of carbon tetrachloride solutions.

(5) The aspiration-coefficient of bromine from nitrobenzene is about one-half of that from carbon tetrachloride.

CEYLON MEDICAL COLLEGE,
COLOMBO.

II.—iso*Dibenzoylglucoxylose.*

By FRANK TUTIN.

IN recent communications (T., 1914, **105**, 767, 1062) Power and Salway described the isolation from the leaves of *Daviesia latifolia* of a new, crystalline, bitter substance, dibenzoylglucoxylose. This substance proved to be the dibenzoyl derivative of a new disaccharide, glucoxylose, and represented a class of compound not previously known to occur in nature.

The present author recently had occasion to prepare a considerable quantity of dibenzoylglucoxylose from the material contained in the mother liquors of the product isolated by Power and Salway. During the course of the purification of this material it was noted that the crystalline product was not homogeneous. It was therefore subjected to a prolonged process of fractional crystallisation from water, from dilute alcohol, and from ethyl acetate. By this means a substance was eventually isolated which melted 20° higher than dibenzoylglucoxylose, and, since it is isomeric with the latter, it has been named iso*dibenzoylglucoxylose*. The amount of this substance isolated in a state of purity was not large, owing to the difficulty of separating it from dibenzoylglucoxylose, but it was evident that an appreciable quantity of it was present.

*iso*Dibenzoylglucoxylose crystallises from water or ethyl acetate in colourless needles, and is more sparingly soluble in these solvents than dibenzoylglucoxylose. It melts at 173—174°, and a mixture of it with the latter (m. p. 152—153°*) melts at 138—143°:

0·1106 gave 0·2340 CO_2 and 0·0575 H_2O. C = 57·7; H = 5·7.

$C_{25}H_{28}O_{12}$ requires C = 57·7; H = 5·4 per cent.

0·2102, made up to 20 c.c. with methyl alcohol, gave α_D −0°8′ in a 2-dcm. tube, whence $[\alpha]_D$ −6·3°.

* Power and Salway (*loc. cit.*) gave the melting point of dibenzoylglucoxylose as 147—148°, but the present author finds that after this material has been crystallised two or three times from ethyl acetate the melting point is raised to 152—153°.

The specific rotation of dibenzoylglucoxylose was determined under identical conditions, and found to be $[\alpha]_D$ −105·9°.

It is evident, therefore, that the new substance is an isomeride of dibenzoylglucoxylose. Its properties are similar to those of the latter compound, and it possesses a bitter taste.

Penta-acetylisodibenzoylglucoxylose was prepared, but the amount available was too small for analysis. It is insoluble in water, very sparingly so in alcohol, but very readily soluble in ethyl acetate. From a mixture of the last-mentioned two solvents it crystallises in small, colourless needles, which melt at 173—174°.

In their first communication (*loc. cit.*, p. 773) Power and Salway recorded the isolation from *Daviesia latifolia* of a small quantity of a quercetin glucoside which was considered to be probably identical with rutin. This small amount of substance, however, appeared to differ from rutin in two respects, namely, it was stated to be readily soluble in alcohol, and to contain four, instead of three, molecules of water of crystallisation. A considerable quantity of this glucoside (about 25 grams) has now been isolated. After recrystallisation from hot water it was found to be very sparingly soluble in alcohol, and was identical with rutin in all its properties. On analysis, the air-dried substance was found to possess the formula $C_{27}H_{30}O_{16},3H_2O$. (Found, C=48·8; H=5·5. Calc., C=48·8; H=5·4 per cent.)

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

III.—*A New Method of Preparing Alkylated Sugars.*

By WALTER NORMAN HAWORTH.

THE investigations conducted in these laboratories during the past twelve years on the alkylated sugars have been directed to the elucidation of the constitution of the simple carbohydrates and their derivatives.

The utility of these sugar ethers has hitherto been restricted by the comparative inaccessibility of the compounds, due to the labour and expense involved in their preparation. For this reason the detailed study of the alkylated disaccharides has long been deferred, whilst the application of the alkylated monosaccharides for purposes of synthetic work has been difficult of realisation. Similarly, the general investigation of the action of enzymes on methylated

sugars, on a scale adequate to the importance of the subject, has had to be postponed until a simplification in the mode of preparation could be introduced.

The present research was undertaken with a view to render these sugar derivatives more readily available for the purposes enumerated. This intention has been realised in so far as it is now possible, by applying the working methods hereafter described, to expedite the production of the alkylated sugars, and also to prepare them in greater variety and at an expense which corresponds with a reduction of the former cost by about four-fifths.

The procedure hitherto adopted for the preparation of the alkylated sugars depends upon the employment of the expensive alkyl iodides and dry silver oxide (Purdie and Irvine, T., 1903, **83**, 1021); and, moreover, the necessity for finding a suitable solvent for the sugar, in the initial stages of the reaction, further circumscribes the applicability and efficiency of the method. The choice of these reagents has, however, been abundantly justified by the results, since it has been established that, under these mild experimental conditions, profound changes, such as racemisation, the Walden inversion, or the interconversion of glucosides, do not occur. Hence these results have been used as a standard for comparison in the present work, wherein somewhat more drastic reagents have found application.

It has now been observed that the substitution of alkyl sulphates and commercial sodium hydroxide, in an aqueous medium, for the expensive reagents formerly used, is attended with many advantages; and whilst the success of the operation is governed to a remarkable degree by the conditions of the experiment, no detrimental effect due to the introduction of alkali hydroxide is apparent, the sugar derivatives isolated having the optimum rotation values in every case where a comparison with known values is possible.

In adapting the experimental conditions to the requirements of the sugar group the guiding principles to be followed were, first, that during the alkylation process the existence, even locally, of an acid system should be avoided, as this, even at comparatively low temperatures, tends to induce changes of a hydrolytic character. Secondly, at no stage of the operations should there be a strongly alkaline system, as in this case the possibility of the formation of complex enolic derivatives, resins, and polysaccharides presents itself (Nef, *Annalen*, 1914, **403**, 204). The conditions have been satisfactorily adjusted to meet these requirements, and the complete experimental details are described on p. 11.

Examples representing almost every type of optically active

hydroxyl compound in the aliphatic series have been chosen, and the derivatives obtained from these are tabulated below:

Sucrose → heptamethyl and octamethyl sucrose.

Methyl glucoside → tetramethyl, trimethyl, and (probably) dimethyl methylglucoside.

Methyl mannoside → tetramethyl, trimethyl, and probably dimethyl methylmannoside.

Methyl galactoside → tetramethyl, trimethyl, and probably dimethyl methylgalactoside.

Salicin → dimethyl, and probably trimethyl and tetramethyl salicin.

Tartaric acid → α-hydroxy-β-methoxysuccinic acid.

Dextrose → alkylated methylglucosides.

Lactose → alkylated lactosides.

Mannitol → various alkylated mannitols up to the pentamethyl derivative.

The derivatives of mannitol will be referred to fully in a subsequent paper, but it may here be mentioned that in this case, as well as in others now described, it has been substantiated that the introduction of methyl groups in a sugar-chain proceeds in definite stages, certain hydroxyl groups displaying a tendency to undergo etherification preferentially, and that homogeneous products, representing the intermediate stages in the alkylation process, may be isolated and definitely characterised. In this respect the present mode of preparation possesses an advantage, in that the use of silver oxide appears to result in a mixture of unchanged and partly alkylated material, which is complex and difficult to separate.

Although the account of the method applied in the course of this work refers exclusively to methyl sulphate, it is intended to apply it to "ethylation," and to the use of the higher alkyl sulphates, in the hope of obtaining the higher homologues of the sugar ethers, which may conceivably be capable of better characterisation than the methyl derivatives. The preparation of these higher ethers by the silver oxide method is excluded by the fact that at the boiling point of the higher alkyl iodides silver oxide functions as an oxidising agent.

For the first time the completely methylated sucrose, namely, octamethyl sucrose, has been obtained in a condition sufficiently pure to admit of its characterisation by physical methods. Curiously enough, the reagents recommended in this paper only carry the alkylation of sucrose to the stage of the heptamethyl compound, and this has been carefully described. Whilst this is so, yet this stage is reached in one alkylation, when the product becomes sparingly soluble in sodium hydroxide, and forms an oily layer

above the solution. It is necessary, in order to advance the material to the octamethyl stage, to have recourse to the use of methyl iodide and silver oxide for the introduction of the one remaining methoxyl group. Heptamethyl sucrose readily dissolves in methyl iodide, and only two treatments with this reagent are required.

Experimental.

The apparatus designed for the process of alkylation with methyl sulphate and sodium hydroxide consists in a wide-necked flask fitted with a cork, and provided with two dropping funnels, a water condenser, and an arrangement for stirring mechanically. The sugar or sugar derivative is dissolved in the minimum amount of water, and the flask surrounded by a water-bath, which is maintained at 70°. An excess of the alkylating reagents, amounting to three times the quantity theoretically required, is then added slowly through the two dropping funnels, one of which is reserved for methyl sulphate, and the other for a 30 per cent. solution of commercial sodium hydroxide, the mixture being vigorously stirred during the operation, which is complete in the course of an hour; subsequently the temperature of the bath is raised to 100° for half-an-hour. The rate of admission of either reagent to the vessel in which the reaction is proceeding is determined by the fact that a slight alkalinity must be maintained throughout. This condition should likewise obtain at the end of the reaction, in order that any unchanged methyl sulphate may be destroyed during the boiling operation, and for this reason the proportion of alkali used should be slightly greater than that of methyl sulphate.

The product, on cooling, is extracted twice with chloroform, the extract dried, and the chloroform distilled. The residue may be subjected to a similar alkylation process if this is necessary for the purpose in hand, half the previous quantities being employed. In most cases the experience has been that the material remaining in the aqueous residues after extraction with chloroform is practically negligible. This partly methylated residue may also be dealt with by concentrating the aqueous solution which has previously been rendered neutral, filtering the separated salt through linen, and submitting the filtrate to a further treatment with the alkylating reagents. The quantities of the reagents requisite for this purpose may be approximately judged by estimating the amount of material already recovered in the chloroform extracts.

Methylation of Sucrose: Heptamethyl Sucrose, $C_{12}H_{14}O_3(OH)(OMe)_7$, *and Octamethyl Sucrose,* $C_{12}H_{14}O_3(OMe)_8$.

From 20 grams of pure sucrose, 15 grams of the heptamethyl ether were obtained after one alkylation. This distilled constantly at 191—195°/0·18 mm. as a colourless, viscid syrup, and gave the following analytical results:

0·1921 gave 0·3633 CO_2 and 0·1418 H_2O. C=51·58; H=8·20.
0·1874 ,, 0·7180 AgI. OMe=50·5.
$C_{19}H_{36}O_{11}$ requires C=51·81; H=8·18; OMe=49·3 per cent.

The physical constants were determined as below:

n_D 1·4656; D_4^{25} 1·1654; M_D 104·49 (M_D calc.=103·49).
$[\alpha]_D$ +68·5° in methyl alcohol (c=5·585).

Using methyl sulphate as the reagent it was not found possible to increase appreciably the methoxyl content of heptamethyl sucrose. This seems to be due to the sparing solubility of the ether in sodium hydroxide. It was therefore found necessary to revert to the use of methyl iodide, in which heptamethyl sucrose readily dissolves, and two treatments with this reagent and silver oxide were necessary to methylate the remaining hydroxyl group in the molecule. The effect of the introduction of this last methyl group was markedly shown in the diminution of the boiling point and of the refractive index, and an increase in the mobility of the product. This was isolated as a slightly viscid, colourless liquid, distilling constantly at 176°/0·05 mm.:

0·1622 gave 0·3133 CO_2 and 0·1242 H_2O. C=52·68; H=8·50.
0·1306 ,, 0·5355 AgI. OMe=54·12.
$C_{20}H_{38}O_{11}$ requires C=52·86; H=8·37; OMe=54·6 per cent.

The physical constants determined are as follows:

n_D 1·4588; D_4^{20} 1·1406; M_D 108·77 (M_D calc.=108·23).
$[\alpha]_D$ in methyl alcohol (c=7·345) +69·3°.
$[\alpha]_D$ in acetone (c=6·782) +66·8°.

It will be seen by comparison of the optical and analytical data with the values given in a previous communication by Purdie and Irvine (T., 1905, **87**, 1028), that the material has now been obtained in a condition of purity. A larger quantity of the substance has since been prepared with a view to the determination of the constitution of sucrose from an examination of the hydrolytic products of the octamethyl ether.

Methylation of α-Methyl Glucoside: Tetramethyl α-Methylglucoside, $C_6H_7O(OMe)_5$, *and the Corresponding Sugar, and of Trimethyl α-Methylglucoside,* $C_6H_8O_2(OMe)_4$.

The chloroform soluble extract (20 grams), obtained by a single alkylation of 25 grams of methyl glucoside, was fractionated into three portions. The first of these was pure tetramethyl α-methylglucoside, which distilled at 108°/0·1 mm. as a colourless, mobile oil:

n_D 1·4454; D_4^{20} 1·1082*; $M_D = 60·14$ (M_D calc. = 60·65).

The identity of this fraction with the substance previously described by Purdie and Irvine (T., 1904, **85**, 1059) was proved by its conversion into the very characteristic, crystalline sugar, tetramethyl glucose. The hydrolysis was effected in the usual way, and the free sugar obtained in long, colourless needles, melting at 84°. This showed mutarotation, and finally attained the value $[\alpha]_D$ +84·5° in aqueous solution ($c = 1·6$), which is in good agreement with the rotation previously recorded (*loc. cit.*) (Found, OMe = 50·84. $C_{10}H_{20}O_6$ requires OMe = 52·54 per cent.).

The refractive index of the superfused sugar was determined, and this was identical with the value shown by a specimen prepared by Purdie and Irvine, namely, $n_D = 1·4588$.

The second fraction, distilling at 130°/0·13 mm., was a viscid, colourless oil; the analytical, physical, and other data indicate that this was trimethyl α-methylglucoside (compare Purdie and Bridgett, T., 1903, **83**, 1037) (Found, OMe = 51·21. $C_{10}H_{20}O_6$ requires OMe = 52·54 per cent.):

n_D 1·4583; D_4^{20} 1·158; M_D 55·63 (M_D calc. = 55·91).

$[\alpha]_D$ +160·3° in methyl alcohol ($c = 2·823$).

The third fraction was very viscid, but quite colourless, and distilled at 140—150°/0·07 mm., and, from its methoxyl content and refractive index (n_D 1·4648), it would appear to be a mixture of dimethyl and trimethyl α-methylglucosides (Found, OMe = 45·5. $C_6H_9O_3(OMe)_3$ requires OMe = 41·9; $C_6H_8O_2(OMe)_4$ requires OMe = 52·5 per cent.).

Methylation of α-Methyl Mannoside: Tetramethyl α-Methylmannoside and Trimethyl α-Methylmannoside.

One alkylation of 14 grams of α-methyl mannoside yielded 10 grams of material soluble in chloroform, which was twice fractionated under diminished pressure. The first fraction, distilling at 108—110°/0·1 mm. and having $n_D = 1·4497$, crystallised com-

* Purdie and Irvine's value.

pletely on nucleating with a specimen of tetramethyl α-methylmannoside, and melted at 37—38°, no depression of the melting point being observed when the crystals were mixed with those of the specimen previously obtained by Irvine and Moodie (T., 1905, **87**, 1465). Its rotation in ethyl alcohol ($c=4{\cdot}475$) showed $[\alpha]_D$ +76·4°, the value previously recorded being +75·5°.

The second fraction distilled at 150°/12 mm. as a viscid, colourless oil, showing $n_D=1{\cdot}4583$:

0·1147 gave 0·4538 AgI. OMe=52·2.

$C_6H_8O_2(OMe)_4$ requires OMe=52·5 per cent.

The third fraction, distilling at 155—162°/12 mm. and showing $n_D=1{\cdot}4650$, corresponds with the similar fraction obtained on alkylating α-methyl glucoside. It consists of a mixture of dimethyl and trimethyl α-methylmannosides.

Methylation of Methylgalactoside: Tetramethyl Methylgalactoside and Trimethyl Methylgalactoside.

The initial material consisted of a mixture of about equal amounts of α- and β-methyl galactosides. The chloroform extract yielded on distillation three fractions.

The first of these distilled at 135—140°/12 mm. as a colourless, mobile oil, having $n_D=1{\cdot}4520$, and this gave analytical figures corresponding with tetramethyl methylgalactoside (compare Irvine and Cameron, T., 1904, **85**, 1071) (Found, OMe=60·2. $C_{11}H_{22}O_6$ requires OMe=62·0 per cent.).

Fraction II, distilling at 150—154°/12 mm., was slightly more viscid than the above, and showed $n_D=1{\cdot}4568$ and $[\alpha]_D$ +48·7° in ethyl alcohol ($c=3{\cdot}1$). This material consisted of trimethyl α- and β-methylgalactosides (Found, OMe=52·6. $C_6H_8O_2(OMe)_4$ requires OMe=52·5 per cent.).

The third fraction, which was small in amount, distilled about 165°/12 mm., and showed $n_D=1{\cdot}4640$. A methoxyl estimation indicated that this contained dimethyl and trimethyl α- and β-methylgalactosides.

Methylation of Salicin: Dimethyl Salicin, $C_{13}H_{13}O_2(OH)_3(OMe)_2$.

The chief product isolated as the result of one treatment of salicin (10 grams) with the alkylating agents appears to be the dimethyl ether. This crystallised on evaporation of the chloroform extract, and after draining on porous tile and recrystallising from a mixture of ethyl acetate and light petroleum, it melted at 122°. It crystallises in slender, colourless prisms, and is lævorotatory, having about the same specific rotation as salicin:

0·0868 gave 0·1821 CO_2 and 0·0560 H_2O. C = 57·21; H = 7·17.
0·1310 „ 0·2055 AgI. OMe = 20·7.
$C_{16}H_{22}O_7$ requires C = 57·32; H = 7·01; OMe = 19·7 per cent.

On extraction of the porous tiles with chloroform, and evaporation of the extract, a syrupy residue remained, which failed to crystallise. This distilled under 0·2 mm. pressure (bath at 220°) as a colourless syrup, which slowly deposited crystals. These were, however, too small in amount to purify, but a methoxyl estimation indicated the presence of three or four methoxyl groups in the salicin molecule, thus showing that alkylation had proceeded beyond the dimethyl ether stage (compare Irvine and Rose, T., 1906, **89**, 814).

Methylation of Tartaric Acid: α-Hydroxy-β-methoxysuccinic Acid, $CO_2H{\cdot}CH(OH){\cdot}CH(OMe){\cdot}CO_2H$.

The application of the method of alkylation recommended in this paper to the case of tartaric acid yielded a somewhat unexpected result, in that the only product isolated in a condition of purity was *α-hydroxy-β-methoxysuccinic acid.* In order to isolate the material formed in this alkylation process, it was necessary to neutralise the alkaline solution with sulphuric acid and evaporate it on the water-bath. The concentrated liquid was acidified and extracted with ether for a prolonged period by means of the Hagemann apparatus. The ethereal extract yielded a syrup which eventually crystallised. The solid was drained on porous tile and recrystallised from much ether, in which it is sparingly soluble. It forms flat, colourless prisms, melting at 174°, and having $[\alpha]_D$ +45·4° in aqueous solution ($c = 1·85$).

The specific rotation is thus the mean of the values recorded for tartaric acid, +14·52° (Landolt, *Ber.*, 1873, **6**, 1075), and dimethoxysuccinic acid, +76·63° (Purdie and Irvine, T., 1901, **79**, 962). The addition of ammonium molybdate to the aqueous solution effects an exaltation of the rotation value:

0·0433 gave 0·0590 AgI. OMe = 17·6.
$C_5H_8O_6$ requires OMe = 18·9 per cent.

Titration: 0·1850 required 0·0885 NaOH for neutralisation, whilst this amount of an acid, $C_5H_8O_6$, should require 0·0896 NaOH.

Methylation of Dextrose and Lactose.

As examples of the alkylation of the reducing sugars, dextrose and lactose were selected. The temperature in the initial stages of the reaction was, in these cases, maintained at 50°. Products derived from both these sugars were isolated in the usual way, and

these were distilled and found to be glucosidic in character. It is therefore established that the alkylated glucosides, probably mixtures of α- and β-forms, can be prepared from the parent sugar directly by the methyl sulphate process, although the yield is not quite so good as in the case of the preparation of ethers from the glucosides. The product derived from dextrose distils at the same temperature as tetramethyl methylglucoside, and has the same refractive index. The product obtained from lactose distils at about 170°/0·05 mm., and has n_D 1·4588, and therefore is comparable with octamethyl sucrose. β-Methyl glucoside has, apparently, been prepared by Maquenne (*Bull. Soc. chim.*, 1905, [iii], **33**, 469) by the agency of methyl sulphate, but, so far as one is aware, no attempt to prepare the alkylated glucosides by this method has before been made.

The author wishes to reserve the substances described in this paper for further work. He also desires to thank the Carnegie Trust for a research grant for materials, and to express his indebtedness to Prof. Irvine for valuable advice, and to Miss Grace C. Leitch for her assistance.

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IV.—*Organo-derivatives of Bismuth. Part II. The Stability of Derivatives of Quinquevalent Bismuth.*

By Frederick Challenger and Charles Frederick Allpress.

In a previous communication (T., 1914, **105**, 2211) it was stated that certain derivatives of quinquevalent bismuth are characterised by the ease with which they can be degraded to compounds in which bismuth functions as a triad. For example, it was not found possible to prepare tetraphenylbismuthonium bromide or triphenylethylbismuthonium bromide; moreover, triphenylbismuthine dibromide and tri-α-naphthylbismuthine dibromide readily eliminate aryl bromide under the influence of heat.

This led to an investigation of the stability of tertiary bismuthine dihaloids containing dissimilar halogen atoms, since the question as to which of these halogens would be eliminated in union with an aryl radicle seemed to be of interest.

Attempts were therefore made to prepare additive products of triphenyl- and tri-α-naphthyl-bismuthine, with iodine, iodine

chloride, and iodine bromide, and also of triphenylbismuthine with cyanogen, cyanogen iodide, cyanogen bromide, and cyanamide.

When triphenylbismuthine and iodine monobromide or iodine monochloride interact, no additive product can be isolated, but iodobenzene and either diphenylbromobismuthine or diphenylchlorobismuthine (see p. 19) are produced in yields which approach closely to those demanded by the equation:

$$BiPh_3 + IX = BiPh_2X + PhI.$$

Chlorobenzene or bromobenzene could not be detected. Similarly, cyanogen iodide gives iodobenzene and *diphenylcyanobismuthine*, which decomposes at about 210°.

The reaction of triphenylbismuthine with iodine is somewhat complicated, and certain points in this connexion yet remain to be elucidated, but owing to the inability of one of us to continue the investigation the results obtained up to the present may briefly be summarised.

In ether or light petroleum solution no di-iodide appears to be formed (compare Gillmeister, *Ber.*, 1897, **30**, 2843), the products of the reaction being diphenyliodobismuthine, iodobenzene, and a red powder containing much organic matter and more than 50 per cent. of iodine.

The red compound is also obtained when iodine is added to a solution of diphenyliodobismuthine, so is probably a product of a secondary reaction. It cannot be triphenylbismuthine di-iodide, since this contains only about 26 per cent. of iodine.

Moreover, the fact of the formation of diphenyliodobismuthine and iodobenzene points to the extreme instability of such a substance. The results obtained with iodine and tri-α-naphthylbismuthine also support this conclusion. The evidence obtained up to the present points strongly in one direction, but owing to the existence of such compounds as triphenylarsine tetraiodide, Ph_3AsI_4, and tri-*p*-tolylarsine tetraiodide, $(C_7H_7)_3AsI_4$ (Michaelis, *Annalen*, 1902, **321**, 203), further discussion is undesirable until these compounds have been prepared for the purposes of comparison.

Gillmeister mentions that iodobenzene, bismuth oxyiodide, and diphenyliodobismuthine are obtained when triphenylbismuthine dichloride and potassium iodide interact and the mixture is poured into water. We have confirmed these results, but find that the red compound referred to above is also a product of the reaction.

The action of iodine monochloride and monobromide on tri-α-naphthylbismuthine is similar to that on the triphenyl compound. No additive product was isolated, but α-iodonaphthalene in yields somewhat below the theoretical was obtained.

With iodine and tri-α-naphthylbismuthine the products are bismuth iodide, α-iodonaphthalene (isolated as dichloride), unchanged bismuthine, and (probably) di-α-naphthyliodobismuthine.

The results so far described, excluding those with iodine, show that when two dissimilar halogen atoms, and, in the case of triphenylbismuthine, cyanogen iodide, enter into reaction with a tertiary aromatic bismuthine the more negative atom or group remains attached to bismuth, whilst iodine is eliminated as aryl iodide. In the case of tri-α-naphthylbismuthine, since the yields of α-iodonaphthalene are not quite quantitative, the formation of some α-bromo- or α-chloro-naphthalene is not absolutely excluded, but seems improbable.

The action of iodine haloids on unsymmetrical (or mixed) bismuthines is being investigated. It might be expected that iodine, being a comparatively positive element, would be eliminated in union with the most strongly negative or unsaturated hydrocarbon radicle present.

In a preliminary experiment diphenyl-α-naphthylbismuthine was treated with iodine monobromide, and α-iodonaphthalene was detected in the solution.

The interaction of diphenylbromobismuthine and iodine chloride is also instructive, a yield of iodobenzene 77 per cent. of that required by the equation $Ph_2BiBr + ICl = PhBiClBr + PhI$ being obtained.

As regards the experiments with cyanogen and its derivatives it might be expected that the unknown compound $Ph_3Bi(CN)_2$ would be very stable owing to the strongly negative nature of both the cyano- and the phenyl group. Under the conditions employed up to the present, however, cyanogen does not react with triphenylbismuthine; moreover, under conditions in which the iodide readily reacts with triphenylbismuthine, cyanogen bromide has no action.

Von Braun (*Ber.*, 1900, **33**, 1438, 2728; 1902, **35**, 1279; 1903, **36**, 1196; 1907, **40**, 3914, 3933) has shown that cyanogen bromide is without action on triphenylamine even when heated in sealed tubes, although it reacts with tribenzylamine. With aliphatic or aliphatic-aromatic amines an unstable additive product is obtained, which decomposes so as to yield alkyl or aryl bromide and a substituted cyanamide.

Unsaturated radicles such as allyl are particularly easily eliminated as bromide.

Cyanamide, which might have been expected to yield aniline and diphenylcyanobismuthine when heated with triphenylbismuthine, polymerised to dicyanodiamide without otherwise reacting.

Experimental.

Diphenylchlorobismuthine.

Marquardt (*Annalen*, 1889, **251**, 326) states that diphenylchlorobismuthine, $BiPh_2Cl$, appears to be formed by the interaction of triphenylbismuthine and bismuth chloride in glacial acetic acid or ethyl acetate, but that he was unable to crystallise it.

Since one of us has observed that triphenylbismuthine is decomposed by glacial acetic acid, and since diphenylchlorobismuthine is decomposed by water or alcohol (both frequently present in ordinary ethyl acetate) the reason for this non-success may not be far to seek. An ethereal solution of 2·5 grams of triphenylbismuthine (2 mols.) was treated with 1·3 grams of bismuth chloride, likewise dissolved in anhydrous ether. Three grams of colourless crystals, melting at 184—185°, were deposited, and on recrystallisation from benzene the melting point was unchanged.

The results of analysis indicate the presence of traces of phenyldichlorobismuthine:

0·3727 gave 0·2202 Bi_2O_3. Bi = 52·94.*

$C_{12}H_{10}ClBi$ requires Bi = 52·33 per cent.

$C_6H_5Cl_2Bi$ „ Bi = 58·43 „ „

Diphenylchlorobismuthine forms colourless crystals fairly readily soluble in dry benzene, toluene, or chloroform, but much less so in ether or light petroleum.

Alcohol and moist solvents cause decomposition as with all compounds of the type BiR_2X and $BiRX_2$. On keeping in a sealed tube gradual decomposition occurs, and benzene is produced. Concentrated hydrochloric acid readily liberates benzene.

Action of Iodine Monochloride on Triphenylbismuthine.

Five grams of triphenylbismuthine in dry ether were treated with 1·85 grams of iodine chloride (1 mol.) in the same solvent. A brownish-yellow turbidity was produced, which quickly disappeared, pale yellow crystals (A, 3·35 grams) separating simultaneously. These melted at 182—183° after being recrystallised, and did not depress the melting point of diphenylchlorobismuthine. On evaporating the decanted ether and treating the oily residue with light petroleum, a further quantity of the crystals was obtained (B, 0·8 gram). The theoretical yield of diphenylchlorobismuthine is 4·5 grams. Deposits A and B contained traces of iodine.

On removal of the light petroleum the residual oil, when treated with chlorine in chloroform solution, gave 2·65 grams of iodobenzene dichloride, whereas the theoretical yield is 3·1 grams.

* A second estimation gave = 52·91.

In another experiment 5 grams of triphenylbismuthine were treated with slightly more than 2·3 grams (1·3 mols.) of iodine chloride. Deposits A_1 (3·25 grams) and B_1 (1·2 grams) were obtained as before, and the yield of iodobenzene dichloride was 3·9 grams. Deposit A_1 contained practically no iodine, but B_1 contained relatively large amounts in comparison with B.

Action of Iodine Monobromide on Triphenylbismuthine.

Iodine bromide (2·35 grams; 1 mol.) dissolved in anhydrous ether was gradually added to triphenylbismuthine (5 grams) in the same solvent. A brownish-yellow turbidity, disappearing on shaking, was produced, and yellow crystals were deposited. These melted at 154°, and after recrystallisation from chloroform, sharply at 157°. The total quantity obtained was 4·6 grams, the theoretical yield of diphenylbromobismuthine being 5 grams.

Fractional extraction of the crystals with hot benzene gave deposits melting at 156—157°, 156—157°, 148°, and 157°. The third deposit after one recrystallisation melted at 155—157°. Further recrystallisation of these deposits produced no change in melting point, so that the presence of compounds other than diphenylbromobismuthine (m. p. 157—158°), except in traces, is excluded.

The ethereal solution was distilled, and a further deposit of diphenylbromobismuthine removed by means of cold chloroform or ether. The iodobenzene remaining in the chloroform was converted into the iododichloride. The yield was 2·95 grams.

Action of Cyanogen Iodide on Triphenylbismuthine.

When 5 grams of triphenylbismuthine and 2·2 grams of cyanogen iodide ($1\frac{1}{4}$ mols.) were heated with benzene under a reflux condenser, 3·2 grams of a yellow solid separated. On distilling off the benzene and treating the oily residue with light petroleum, 0·7 gram of the yellow solid remained.*

On removing the petroleum, adding chloroform, and passing chlorine, 2·95 grams of iodobenzene dichloride were obtained.

The solid substance was recrystallised from hot alcohol, only a very small, insoluble residue remaining:

0·2396 + 10·1 c.c. 0·13*N*-$AgNO_3$ required 7·3 c.c. *N*/10-NH_4CNS.

CN = 6·29.

$C_{13}H_{10}NBi$ requires CN = 6·71 per cent.

* This deposit contained a certain amount of an iodine compound. On crystallising from benzene, however, a very small quantity of yellow solid remained undissolved, whilst the solution deposited white crystals identical with the main product. The formation of the yellow insoluble substance containing iodine is probably due to the excess of cyanogen iodide.

Diphenylcyanobismuthine forms colourless needles, resembling glass-wool, and smelling faintly of hydrocyanic acid. These melt and decompose at about 210°, and are sparingly soluble in hot alcohol or benzene, still less so in ether or light petroleum. On concentrating the alcoholic solution, hydrocyanic acid is evolved (recognised by conversion into ammonium thiocyanate), and on cooling, triphenylbismuthine is deposited. Warm concentrated hydrochloric acid liberates benzene and hydrocyanic acid; warm sodium hydroxide forms sodium cyanide and a yellow, insoluble substance, which is being further investigated. With silver nitrate solution diphenylcyanobismuthine readily gives silver cyanide.

Action of Iodine on Triphenylbismuthine.

A. *In Dry Ethereal Solution.*—When 10 grams of triphenylbismuthine were treated with 5·8 grams of iodine (1 mol.) a red precipitate was produced. The ether containing a yellow solid in suspension was poured off, and the red precipitate (3·5 grams) washed with dry ether.

(The yellow solid in ethereal suspension melted at 134°. Diphenyliodobismuthine forms yellow needles, melting at 133°.) After distilling about half of the ether a solid separated, which melted at 131°; this was removed, and the ether completely evaporated. The residual oil still contained bismuth. Its chloroform solution was treated with a very slight excess of bromine, in the hope of removing any triphenylbismuthine as triphenylbismuthine dibromide (m. p. 122°). The crystals which separated, however, melted after one recrystallisation at 201—202°, and did not depress the melting point of a specimen of phenyldibromobismuthine.

Their formation was obviously due to the action of bromine on diphenyliodobismuthine thus: $BiPh_2I + Br_2 = BiPhBr_2 + PhI$.

The chloroform mother liquor gave rise to 5·5 grams of iodobenzene dichloride, corresponding with 4·1 grams of iodobenzene. The theoretical yield to be expected from the equation

$$BiPh_3 + I_2 = BiPh_2I + PhI$$

is 4·65 grams. Since much iodobenzene was probably produced through the agency of the bromine, the quantity directly obtained by the action of iodine on the bismuthine is seen to be far below the theoretical.

The red precipitate, melting at about 194°, contained much iodine and organic matter, and evolved benzene on treatment with hydrochloric acid. When heated with benzene or chloroform a purplish-black residue, still containing organic matter, and a yellow solution were obtained, which on addition of light petroleum deposited a red solid.

B. *In Ether–Light Petroleum Solution.*—Five grams of triphenylbismuthine were treated with 2·9 grams of iodine. The usual brown turbidity, followed by the deposition of crystals melting at 131—134°, was produced, and the red precipitate, which this time melted at 131°, was also deposited (4·5 grams). A further quantity of yellow crystals melting at 133° was obtained by distilling off the petroleum, after which the solution contained only a trace of solid matter, and gave rise, in the usual way, to 2·4 grams of iodobenzene dichloride, corresponding with 1·8 grams of iodobenzene. The theoretical yield is 2·33 grams.

The red powder was heated with dry benzene, the yellow solution filtered, and allowed to deposit five separate crops of crystals:

Original substance red, m. p. 131°.
1st deposit. Deep red crystals, m. p. 194—198°.
2nd deposit. Paler red crystals, m. p. 130°.
3rd deposit. Orange crystals, m. p. 125°.
4th deposit. Pale yellow crystals, m. p. 127°.
5th deposit. Brown solid, m. p. above 210°.

The substance therefore decomposes on contact with hot benzene and other solvents. If it is extracted with hot dry carbon tetrachloride until the extract is no longer coloured, the residue is brownish-black, and consists principally of bismuth iodide.

Action of Iodine Monochloride on Tri-α-naphthylbismuthine.

Five grams of tri-α-naphthylbismuthine were gradually treated with 1·95 grams (1·4 mols.) of iodine monochloride, both being dissolved in a mixture of ether and chloroform.

The solvent was then partly distilled off, and the yellow deposit collected. It decomposed at about 240°, and probably consisted largely of di-α-naphthylchlorobismuthine, $Bi(C_{10}H_7)_2Cl$. The chloroform–ether filtrate was distilled to dryness, the residual oil removed from a small quantity of dark-coloured solid by means of light petroleum, and the solution diluted with glacial acetic acid, cooled, and treated with chlorine. The weight of iodonaphthalene dichloride (m. p. 55°) obtained was 2·75 grams, the theoretical yield being 3·90 grams.

Action of Iodine Monobromide on Tri-α-naphthylbismuthine.

Tri-α-naphthylbismuthine (2·5 grams) was treated with 0·85 gram (1 mol.) of iodine monobromide, both in chloroform solution. The reaction mixture was worked up in the usual way, and found to yield in addition to 1·1 grams of α-iodonaphthalene dichloride (theoretical yield 1·4 grams) a certain amount of unchanged bismuthine. The principal solid product, although containing traces of iodine,

probably consisted largely of di-α-naphthylbromobismuthine. It was only superficially examined, and is reserved for further investigation.

Action of Iodine on Tri-α-naphthylbismuthine.

One gram of tri-α-naphthylbismuthine in dry benzene was slowly treated with a similar solution of 0·43 gram of iodine, and the brown precipitate was collected. It was free from organic matter, and indistinguishable as regards the action of heat, water, sulphuric acid, or nitric acid, from bismuth iodide.

The benzene was removed from the filtered reaction mixture, and the reddish-yellow residue extracted with cold light petroleum. On evaporation of the extract, and removal of a small quantity of tri-α-naphthylbismuthine, the oily residue was treated with light petroleum and glacial acetic acid, boiled in order to decompose any traces of bismuthine, cooled, and treated with chlorine, when α-iodonaphthalene dichloride (0·45 gram) was obtained.

The residue insoluble in light petroleum weighed 0·5 gram, and contained iodine. It almost certainly consisted of tri-α-naphthylbismuthine and di-α-naphthyliodobismuthine, since on allowing it to remain in the air it developed a strong odour of naphthalene.* On then extracting with cold benzene, tri-α-naphthylbismuthine was obtained, and the residue was bright red, free from organic matter, and indistinguishable from bismuth oxyiodide.

If the substance, when freshly obtained, was extracted with hot benzene and the extract treated with alcohol, pure tri-α-naphthylbismuthine crystallised out. The colourless mother liquors gradually deposited bismuth oxyiodide, indicating the decomposition by alcohol of di-α-naphthyliodobismuthine.

Action of Iodine Monobromide on Diphenyl-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine (0·3 gram) was treated with iodine monobromide (0·13 gram) in chloroform–ether solution. Instant decolorisation took place, and the solvent was distilled off. The residue was treated with light petroleum, the extract filtered, diluted with glacial acetic acid, and treated with chlorine, when about 0·05 gram of α-iodonaphthalene dichloride (m. p. 65—70°) was obtained.

* Compounds of the type BiR_2X decompose on keeping even in closed vessels, or in the presence of alcohol and moist solvents, giving a hydrocarbon and bismuth oxyhaloid (see page 19 and Gillmeister, *Ber.*, 1897, **30**, 2844).

Action of Iodine Monochloride on Diphenylbromobismuthine.

Four grams of diphenylbromobismuthine were covered with dry ether and slowly treated with an ethereal solution of 1·5 grams (1 mol.) of iodine monochloride. A brown turbidity was produced, which on vigorous shaking slowly disappeared.

The insoluble residue (2·60 grams), which contained iodine, melted very indefinitely at about 190°, and was not further examined, since from its method of preparation it seemed very probable that it might contain phenylchlorobromobismuthine, BiPhClBr, bismuth dichlorobromide, $BiCl_2Br$, and similar substances.

The oily residue from the ethereal solution and washings was extracted with cold chloroform, and the solution yielded 1·95 grams of iodobenzene dichloride, the theoretical amount (removal of one phenyl group) being 2·5 grams. The small residue insoluble in chloroform contained no organic matter.

Cyanogen and Triphenylbismuthine.

Cyanogen was passed into 0·9 gram of triphenylbismuthine dissolved in about 10 c.c. of benzene, but no reaction appeared to occur. The liquid was diluted with an equal volume of ether, and the gas again passed, but with the same result. On spontaneous evaporation of the solvent the bismuthine was recovered unchanged. Similar results were obtained in boiling benzene.

Cyanogen Bromide and Triphenylbismuthine.

Five grams of triphenylbismuthine and 1·5 grams of cyanogen bromide (1¼ mol.) were heated in benzene solution for four hours without any separation of the sparingly soluble diphenylcyanobismuthine taking place. In ether there was no action, either on boiling or on allowing to remain for three weeks.

Cyanamide and Triphenylbismuthine.

When 5 grams of triphenylbismuthine and 0·9 gram of cyanamide were heated with benzene a white solid separated, which was free from bismuth. It melted at about 203°, and after recrystallisation from alcohol and light petroleum, at 205—207°. It was obviously dicyanodiamide, and was also obtained when cyanamide alone was heated in benzene.

Since the cyanamide employed was deliquescent and contained traces of dicyanodiamide (quite insufficient, however, to account

for the large amount obtained as above), a portion was treated with ether, in which dicyanodiamide is insoluble, and with phosphoric oxide, filtered, the ether removed, and the dry cyanamide heated with benzene and triphenylbismuthine, but with the same result. No change occurred when cyanamide and triphenylbismuthine were heated in dry ether.

Relative Stabilities of the Triphenylbismuthine Dihaloids.

Owing to the comparatively positive nature of the iodine atom, triphenylbismuthine di-iodide seems to be an extremely unstable substance, which decomposes as soon as formed, eliminating iodobenzene, whereas the corresponding dibromide is much more stable.

The question naturally suggested itself, whether, on account of the stronger negative nature of chlorine, the dichloride would be found to be more stable than the dibromide.

On heating in a sealed tube at 100° the dichloride was unaltered, but on boiling its solution in dry benzene partial decomposition occurred, diphenylchlorobismuthine (see p. 19) separating. The mother liquors yielded unchanged dichloride. The difference in stability is therefore only slight.

Nevertheless, it seemed possible that although the action of magnesium phenyl bromide on triphenylbismuthine dibromide does not give rise to tetraphenylbismuthonium bromide, the corresponding bismuthonium chloride might be obtained from triphenylbismuthine dichloride.

The action of magnesium phenyl bromide on the dichloride led, however, to the formation of derivatives of tervalent bismuth.

The authors are indebted to the Research Fund of the Chemical Society for a grant in aid of this investigation, and to Dr. T. S. Price for allowing the use of his laboratory in the later stages of the work.

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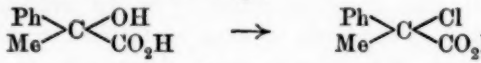
Birmingham.

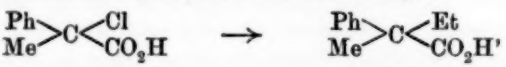
V.—*Conversion of* l-*Phenylchloroacetic Acid into* d-*Diphenylsuccinic Acid.*

By Alex. McKenzie, Harry Dugald Keith Drew, and Gerald Hargrave Martin.

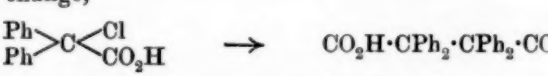
In examining the action of thionyl chloride on the isomeric α-hydroxy-α-phenylpropionic acids, McKenzie and Clough (T., 1910, **97**, 1016) observed that the change,



which takes place at the ordinary temperature, could be utilised for the preparation of the α-chloro-α-phenylpropionic acids without the necessity of isolating the corresponding acid chlorides. The chlorine in those chloro-acids is very loosely bound; it can be displaced with remarkable ease by the action of water. With these facts before us, it appeared likely that a convenient method might be available for the preparation of compounds containing an asymmetric quaternary carbon atom; for example, if α-chloro-α-phenylpropionic acid were acted on by magnesium ethyl iodide, there was a reasonable prospect that the change,



would occur. Accordingly, with the object of studying the action of Grignard reagents on compounds of the type of α-chloro-α-phenylpropionic acid containing a labile halogen atom, some preliminary experiments were conducted with the more readily accessible diphenylchloroacetic acid, prepared from benzilic acid. When this chloro-acid was acted on by magnesium phenyl bromide, and the additive compound then decomposed in the customary fashion, it became clear that some other organic acid was present in addition to triphenylacetic acid, and the conclusion was drawn that the change,



had in all probability also occurred. This particular action was not, however, thoroughly investigated, as it suggested the more interesting stereochemical problem, which is dealt with in the present communication.

The existence of four diphenylsuccinic acids, namely, the *d*-, *l*-, *r*-, and *meso*-forms, is indicated by theory, and of these acids the two optically inactive modifications, the so-called α- and β-forms, are described in the literature; no information is, however, avail-

able as to which of these is the resolvable form. The authors have now been able to obtain the dextrorotatory isomeride by acting on *l*-phenylchloroacetic acid with magnesium phenyl bromide. This action proceeds, as might be expected, in various directions, since the chloro-acid presents a number of points of attack for the Grignard reagent. In the transformation involving the production of *d*-diphenylsuccinic acid, namely,

$$l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \longrightarrow d\text{-}\begin{matrix}C_6H_5\cdot CH\cdot CO_2H\\ CO_2H\cdot CH\cdot C_6H_5\end{matrix},$$

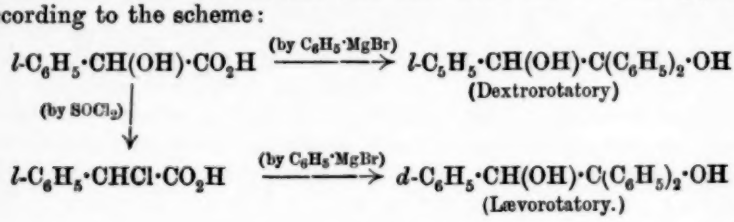
an acid containing two asymmetric carbon atoms is synthesised from an acid containing one such atom, the latter acid combining, as it were, with itself, with the elimination of chlorine. The striking point is that the optical activity does not disappear in this synthesis. The change may be represented as follows:

$$2C_6H_5\cdot CHCl\cdot CO_2H + 4C_6H_5\cdot MgBr =$$
$$C_6H_5\cdot C_6H_5 + 2MgClBr + \begin{matrix}C_6H_5\cdot CH\cdot CO_2MgBr\\ CO_2MgBr\cdot CH\cdot C_6H_5\end{matrix}.$$

$$\begin{matrix}C_6H_5\cdot CH\cdot CO_2MgBr\\ CO_2MgBr\cdot CH\cdot C_6H_5\end{matrix} + 2H_2O = 2MgBr\cdot OH + \begin{matrix}C_6H_5\cdot CH\cdot CO_2H\\ CO_2H\cdot CH\cdot C_6H_5\end{matrix}.$$

The results obtained by the action of magnesium alkyl haloids on *r*-phenylchloroacetic acid and on *r*-phenylbromoacetic acid are recorded in the experimental part. The following compounds were obtained by the action of magnesium phenyl bromide on *l*-phenylchloroacetic acid: diphenyl, *d*-$\alpha\beta$-dihydroxy-$\alpha\beta\beta$-triphenylethane, β-diphenylsuccinic acid, diphenylacetic acid, and *d*-diphenylsuccinic acid. The latter acid was obtained only in very small yield from the mixture of acids resulting from the Grignard action, this mixture consisting of *l*-phenylchloroacetic acid, *r*- and *l*-mandelic acids, diphenylacetic acid, *d*- and *l*- and *meso*-diphenylsuccinic acids. The acid is strongly dextrorotatory, having $[\alpha]_D + 348°$ in ethyl-alcoholic solution; we were, however, unable, with the small quantity at our disposal, to prove the optical purity of this product, so that this value must for the present be given with reserve. Of the two inactive diphenylsuccinic acids, the α-form has the lower melting point. In the case of the isomeric dibromosuccinic acids, the *iso*-form melts at a lower temperature than its inactive isomeride, and it is resolvable into optically active components (McKenzie, T., 1912, **101**, 1196); similarly with the dimethylsuccinic acids, the isomeride of lower melting point is resolvable (Werner and Basyrin, *Ber.*, 1913, **46**, 3229; compare also the case of the $\alpha\alpha'$-dimethyladipic acids examined by Noyes and Kyriakides, *J. Amer. Chem. Soc.*, 1910, **32**, 1057). It is accordingly desirable that the question as to which of the diphenylsuccinic acids is resolvable should be settled.

As already mentioned, *d*-$\alpha\beta$-dihydroxy-$\alpha\beta\beta$-triphenylethane* (lævorotatory) was one of the neutral products of the Grignard action on *l*-phenylchloroacetic acid. Since *l*-phenylchloroacetic acid is obtained from *l*-mandelic acid by means of thionyl chloride (McKenzie and Barrow, T., 1911, **99**, 1910), it is accordingly possible to convert *l*-mandelic acid into both the *d*- and *l*-glycols according to the scheme:



Experimental.

Action of Magnesium Methyl Iodide on r-*Phenylchloroacetic Acid.*

Several experiments on this action were conducted in which the proportion of the Grignard reagent was varied; thus, for phenylchloroacetic acid (1 mol.), magnesium methyl iodide in the proportions of 2, 3, 4, 6, and 7 mols. respectively was employed. In other experiments, where methyl iodide was siphoned into an ethereal solution of phenylchloroacetic acid in contact with an excess of magnesium, there was no improvement, so far as the yield of the diphenylsuccinic acids was concerned, on the customary method of applying the Grignard reagent; on the contrary, the yield of these acids was smaller than usual. The yield of glycols did not increase appreciably when an excess of magnesium alkyl haloid was used. With the proportion of 2, 3, or 4 mols. of magnesium methyl iodide to 1 mol. of the chloro-acid, there was only a slight evolution of gas on the addition of ice to the product of the reaction; on the other hand, with the reagent in the proportion of 6 or 7 mols., the evolution of gas on the addition of ice was vigorous, the Grignard reagent being obviously in excess under these conditions.

From the resulting mixture of acids, β-diphenylsuccinic acid to the extent of from 7 to 11 per cent. was obtained (the percentage yields given here and subsequently are calculated, for convenience, on the basis that the initial halogen acid is transformed into one compound only, namely, the compound under consideration). The α-isomeride was also present, apparently to about the same extent as the β-form, but the amount of it actually isolated in the pure

* McKenzie and Wren (T., 1910, **97**, 473) prepared the dextrorotatory glycol both from methyl *l*-mandelate and from *l*-benzoin. A configurational change was impossible here, and the compound was therefore designated as *l*-.

condition was always very small, owing to the difficulty of separating it from the other acids present. Hydratropic acid was obtained in yields varying from 12 to 15 per cent. when the mixture of acids was subjected to distillation in steam. Even when the reaction took place in the proportion of 3 mols. of the magnesium alkyl haloid to 1 mol. of the chloro-acid, it was quite clear that some of the latter was not attacked, since a comparatively large quantity of mandelic acid was subsequently isolated. Moreover, this chloro-acid which had survived the attack of the Grignard reagent was not entirely hydrolysed during the various operations, and some of it was extracted from the mixture of acids by means of boiling light petroleum. It was observed that the ethereal solution of the mixture of acids was not rendered free from iodine even after it had been shaken several times with sulphurous acid; this behaviour indicated the presence of some unstable iodine compound, possibly phenyliodoacetic acid. When the proportion of magnesium methyl iodide was 4 or more mols. to 1 mol. of the chloro-acid, the iodine which was liberated at the initial stages of the action eventually disappeared as the addition of the reagent proceeded, and there was no liberation of iodine when the additive compounds were decomposed by ammonium chloride. A typical experiment may be described in detail.

The Grignard reagent prepared from 34 grams of methyl iodide (4 mols.) was added drop by drop by means of a siphon to an ethereal solution of 10 grams of *r*-phenylchloroacetic acid (1 mol.). The vigorous action was accompanied by the evolution of an inflammable gas. An oil containing iodine separated at an early stage, and the colour of the iodine disappeared later. After decomposition with ice and ammonium chloride, the aqueous solution was extracted with ether for the purpose of removing the glycols present, whilst the acids were obtained from the aqueous ammoniacal solution by acidification with mineral acid and extraction with ether. The ether was then removed from the latter extract, and hydratropic acid was obtained as a colourless oil by means of distillation in steam; it was converted into its calcium salt. (Found, $H_2O = 9{\cdot}8$. Calc. for $2H_2O$, 9·7 per cent. Ca in anhydrous salt = 11·4. Calc., Ca = 11·8 per cent.) Those acids which were not volatile with steam were extracted with ether, the ether expelled, and the residue extracted with benzene. The white solid which remained undissolved after this treatment was crystallised from ethyl alcohol, from which it separated in fine, silky needles. It consisted of *β*-diphenylsuccinic acid, and melted at 228—230°. (Found, C = 70·5; H = 5·2. Calc., C = 71·1; H = 5·2 per cent. Equivalent, by titration with baryta = 135·7. Calc. =

135·1.) The silver salt was also analysed. (Found, Ag = 44·6. Calc., Ag = 44·6 per cent.) By the crystallisation of the oily acid resulting from the benzene solution, a small quantity of α-diphenylsuccinic acid was eventually isolated; this melted at 181—183°, and, after resolidification, at 219—221°. Small quantities of mandelic and phenylchloroacetic acids were also separated.

The following data regarding the melting point of β-diphenylsuccinic acid are recorded in the literature: 229°, Reimer (*Ber.*, 1881, **14**, 1803), Chalaney and Knoevenagel (*Ber.*, 1892, **25**, 296); 245°, Anschütz and Bendix (*Annalen*, 1890, **259**, 61); 252°, Roser (*Annalen*, 1888, **247**, 152), Ruhemann and Naunton (T., 1912, **101**, 50). According to Reimer (*loc. cit.*), α-diphenylsuccinic acid fuses at 183°, then solidifies, and then melts at 220—221°.

Action of Magnesium Phenyl Bromide on r-*Phenylhalogenacetic Acids.*

An ethereal solution of the Grignard reagent prepared from 37 grams of bromobenzene (4 mols.) was added gradually to an ethereal solution of 12·5 grams of *r*-phenylbromoacetic acid (1 mol.). The following products were isolated: diphenyl, phenol, αβ-dihydroxy-αββ-triphenylethane, diphenylacetic acid, β-diphenylsuccinic acid (1·9 grams), and α-diphenylsuccinic acid (1·8 grams). The latter acid was analysed. (Found, C = 70·8; H = 5·6 Calc., C = 71·1; H = 5·2 per cent. Equivalent, by titration with baryta = 136·2. Calc. = 135·1.)

The amounts of the isomeric diphenylsuccinic acids formed in this experiment were greater than when phenylchloroacetic acid (see below) was employed. This is to be attributed to the fact that the displacement of halogen occurs much more readily with the bromo- than with the chloro-acid.

In three experiments carried out under varying conditions with *r*-phenylchloroacetic acid, the following substances were isolated:

	αβ-Dihydroxy-αββ-triphenylethane.	β-Acid.	α-Acid.	Diphenylacetic acid.
Experiment 1.....	10 per cent.	13 per cent.	1 per cent.	1 per cent.
„ 2.....	20 „	5 „	—	8 „
„ 3.....	17 „	6 „	—	7 „

After the removal of the neutral products of the action, a mixture of acids was obtained as usual. When the ethereal solution of the latter was allowed to evaporate spontaneously, a mixture of β-diphenylsuccinic acid and diphenylacetic acid crystallises. This mixture is easily separated into its components; the residual oil contains the α-acid, together with phenylchloroacetic and mandelic acids.

Action of Magnesium Phenyl Bromide on l-Phenylchloroacetic Acid.

Of the various experiments carried out on this action, the following gave the best results.

l-Phenylchloroacetic acid was prepared by resolving the *r*-acid with morphine according to McKenzie and Clough's method (T., 1908, **93**, 811). The Grignard reagent, prepared from 111 grams of bromobenzene (4 mols.) and 550 c.c. of ether, was added within an interval of fifty minutes to a solution of 30 grams of the *l*-acid (1 mol.) in 80 c.c. of ether, the flask being immersed in ice-cold water during the operation. After warming for fifteen minutes, the mixture was left at the ordinary temperature for twenty-four hours, and then decomposed by a concentrated solution of ammonium chloride. The ethereal solution containing the neutral products was separated from the aqueous layer, which was further extracted twice with ether. The oil resulting from the ethereal solution amounted to about 30 grams, and consisted mainly of diphenyl. After seven days, the crystals which had separated were removed and crystallised from ethyl alcohol. The resulting solid (2·2 grams), which had $[\alpha]_D$ −186° in acetone, and which possibly contained some of the *r*-glycol, was crystallised from methyl alcohol, when 1·6 grams of the pure active glycol were obtained.

d-*αβ-Dihydroxy-αββ-triphenylethane* (*triphenylethylene glycol*), $OH\cdot CHPh\cdot CPh_2\cdot OH$, separates from methyl alcohol in colourless needles and melts at 128°, whereas the dextrorotatory *l*-isomeride melts at 128—129° (McKenzie and Wren, T., 1910, **97**, 480):

0·192 gave 0·5817 CO_2 and 0·1104 H_2O. C=82·6; H=6·4.

$C_{20}H_{18}O_2$ requires C=82·7; H=6·3 per cent.

The compound gave an emerald-green coloration with concentrated sulphuric acid. Its solution in chloroform was lævorotatory:

$$l=2,\ c=1\cdot32,\ \alpha_D -6\cdot02°,\ [\alpha]_D -228°.$$

The aqueous solution of ammonium salts, from which the neutral products had been removed in the manner indicated, was acidified by hydrochloric acid, and the organic acids were then extracted with ether. On expulsion of the ether, an oil (23 grams) was obtained, which gradually solidified partly. The solid (5·5 grams) consisted of a mixture of β-diphenylsuccinic acid and diphenylacetic acid, the separation of which was easy, since the former is practically insoluble in benzene. One gram of β-diphenylsuccinic acid was isolated. (Found, C=71·1; H=5·2. Calc., C=71·1; H=5·2 per cent.) The amount of diphenylacetic acid isolated was 3·1 grams. (Found, equivalent=213. Calc.=212·1.) The melt-

ing point observed was 146°, whereas Jena (*Annalen*, 1870, **155**, 84) gives 145—146°.

The oil from which these acids had been partly separated was dextrorotatory, having $[\alpha]_D$ +17·9° in ethyl-alcoholic solution. A slight excess of sodium hydroxide was added, and the solution boiled, in order to convert any phenylchloroacetic acid present into mandelic acid. After evaporation, the crystals of sodium salt (1·6 grams) which separated had $[\alpha]_D$ +66·8° in aqueous solution. Two further quantities of sodium salt were removed from the filtrate, but these were only slightly dextrorotatory, the values obtained being $[\alpha]_D$ +4° and +3·4° respectively. The sodium salt (1·6 grams) was accordingly recrystallised from water, in which it dissolved readily. 0·7 Gram with $[\alpha]_D$ +127° was obtained. The acid obtained from this by acidification and extraction with ether had $[\alpha]_D$ +287° in ethyl-alcoholic solution; it was crystallised from benzene, in which it is very sparingly soluble. Yield, 0·2 gram.

d-*Diphenylsuccinic acid*, $C_{16}H_{14}O_4$, separates from benzene in colourless, prismatic needles. After drying at 100°, it shrank sharply to a thin core at 170—171°, which was unchanged until 211·5°, when it melted sharply to a clear liquid, from which gas was not evolved. The acid is sparingly soluble in hot water:

0·1107 gave 0·2881 CO_2 and 0·0553 H_2O. C=71·0; H=5·6.

$C_{16}H_{14}O_4$ requires C=71·1; H=5·2 per cent.

Its rotation was determined in ethyl-alcoholic solution:

$l=1$, $c=1·07$, α_D^{15} +3·73°, $[\alpha]_D^{15}$ +348°.

Part of the expense of this investigation was defrayed by a grant from the Government Grant Committee of the Royal Society, to whom our best thanks are due.

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VI.—2 : 4-*Dichlorophenylhydrazine.*

By FREDERICK DANIEL CHATTAWAY and CHARLES FREDERICK BYRDE PEARCE.

FROM the circumstance that 2 : 4-dichlorophenylhydrazine, which should be obtainable from perhaps the most easily made chloro-substituted aniline, has never been described, it might be inferred that its preparation offers some difficulty. This, however, is not the case; it is easily made by the ordinary method, and is a stable,

well-crystallised compound showing the usual behaviour of halogen-substituted aromatic hydrazines, and yielding a series of well-crystallised hydrazides and hydrazones.

2:4-*Dichlorophenylhydrazine*, $C_6H_3Cl_2\cdot NH\cdot NH_2$.

Forty grams of 2:4-dichloroaniline suspended in 200 c.c. of concentrated hydrochloric acid were diazotised by 22 grams of sodium nitrite dissolved in 60 c.c. of water, and the diazonium salt thus formed was reduced by 120 grams of crystallised stannous chloride dissolved in 100 c.c. of concentrated hydrochloric acid.

The hydrochloride of the base, which separated at once as a crystalline precipitate, was washed several times with a saturated solution of sodium chloride, and recrystallised twice from boiling water slightly acidified with hydrochloric acid.

2:4-*Dichlorophenylhydrazine hydrochloride*,

$C_6H_3Cl_2\cdot NH\cdot NH_2,HCl$,

crystallises from aqueous solution in tufts of thin, colourless plates, which decompose in the neighbourhood of 210°:

0·3701 gave 0·7417 AgCl. Cl=49·57.

$C_6H_6N_2Cl_2,HCl$ requires Cl=49·83 per cent.

The base was obtained by adding excess of potassium hydroxide to an aqueous solution of the hydrochloride and extracting with ether, air being carefully excluded.

On distilling off the ether, the base was left as a mass of slender needles. It was recrystallised from ether or light petroleum, in both of which it is readily soluble. It separates from either solvent in slender, colourless, needle-shaped crystals, melting at 94°:

0·5349 gave 0·8631 AgCl. Cl=39·91.

$C_6H_6N_2Cl_2$ requires Cl=40·07 per cent.

When strongly heated alone it slowly decomposes into 2:4-dichloroaniline, *m*-dichlorobenzene, nitrogen, and ammonia, and when oxidised by Fehling's solution or alkaline chromate yields *m*-dichlorobenzene and nitrogen.

Acetyl-2:4-*dichlorophenylhydrazine*, $C_6H_3Cl_2\cdot NH\cdot NH\cdot CO\cdot CH_3$.

2:4-Dichlorophenylhydrazine reacts vigorously with acetic anhydride when the materials are mixed in equivalent amounts, much heat is evolved, and the acetyl compound is formed. This crystallises from alcohol, in which it is moderately soluble, in slender, colourless prisms, melting at 157°:

0·3511 gave 0·4608 AgCl. Cl=32·46.

$C_8H_8ON_2Cl_2$ requires Cl=32·38 per cent.

Propionyl-2:4-dichlorophenylhydrazine,
$C_6H_3Cl_2\cdot NH\cdot NH\cdot CO\cdot C_2H_5$.

This compound, prepared similarly from propionic anhydride, is very readily soluble in chloroform and sparingly so in light petroleum. It crystallises from a mixture of the two in clusters of very small, colourless needles, melting at 102°:

0·4911 gave 0·5958 AgCl. Cl = 30·01.

$C_9H_{10}ON_2Cl_2$ requires Cl = 30·43 per cent.

Benzoyl-2:4-dichlorophenylhydrazine,
$C_6H_3Cl_2\cdot NH\cdot NH\cdot CO\cdot C_6H_5$.

This compound is formed when benzoyl chloride is allowed to act on 2:4-dichlorophenylhydrazine suspended in water, the liberated hydrogen chloride being neutralised by dilute alkali. It crystallises from alcohol, in which it is moderately soluble, in small, colourless, needle-shaped crystals, melting at 168°. (Found, Cl = 25·07. $C_{13}H_{10}ON_2Cl_2$ requires Cl = 25·23 per cent.) Ponzio (*Gazzetta*, 1909, **39**, i, 661) describes the compound as crystallising from benzene in yellow needles, melting at 166°.

Benzaldehyde-2:4-dichlorophenylhydrazone,
$C_6H_3Cl_2\cdot NH\cdot N{:}CH\cdot C_6H_5$.

This compound is formed, with evolution of heat, when alcoholic solutions of equivalent amounts of benzaldehyde and 2:4-dichlorophenylhydrazine are mixed. It is readily soluble in hot alcohol, from which it crystallises in colourless, rhombic plates, melting at 107°:

0·4228 gave 0·4535 AgCl. Cl = 26·53.

$C_{13}H_{10}N_2Cl_2$ requires Cl = 26·76 per cent.

Cinnamaldehyde-2:4-dichlorophenylhydrazone,
$C_6H_3Cl_2\cdot NH\cdot N{:}CH\cdot CH{:}CH\cdot C_6H_5$.

This compound, which is similarly prepared from cinnamaldehyde, is very sparingly soluble in boiling alcohol, but more readily so in boiling acetic acid. It crystallises well from either solvent in pale yellow, four-sided, rhombic plates, melting at 163°:

0·3188 gave 0·3129 AgCl. Cl = 24·28.

$C_{15}H_{12}N_2Cl_2$ requires Cl = 24·36 per cent.

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VII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XI. The Co-ordination of the Rotatory Powers* (a) *of Menthyl Compounds,* (b) *of the Menthones, and* (c) *of the Borneols.*

By Joseph Kenyon and Robert Howson Pickard.

A survey of the rotatory powers of the optically active carbon compounds shows that those of many derivatives of *l*-menthol and *l*-menthylamine exhibit striking regularities.

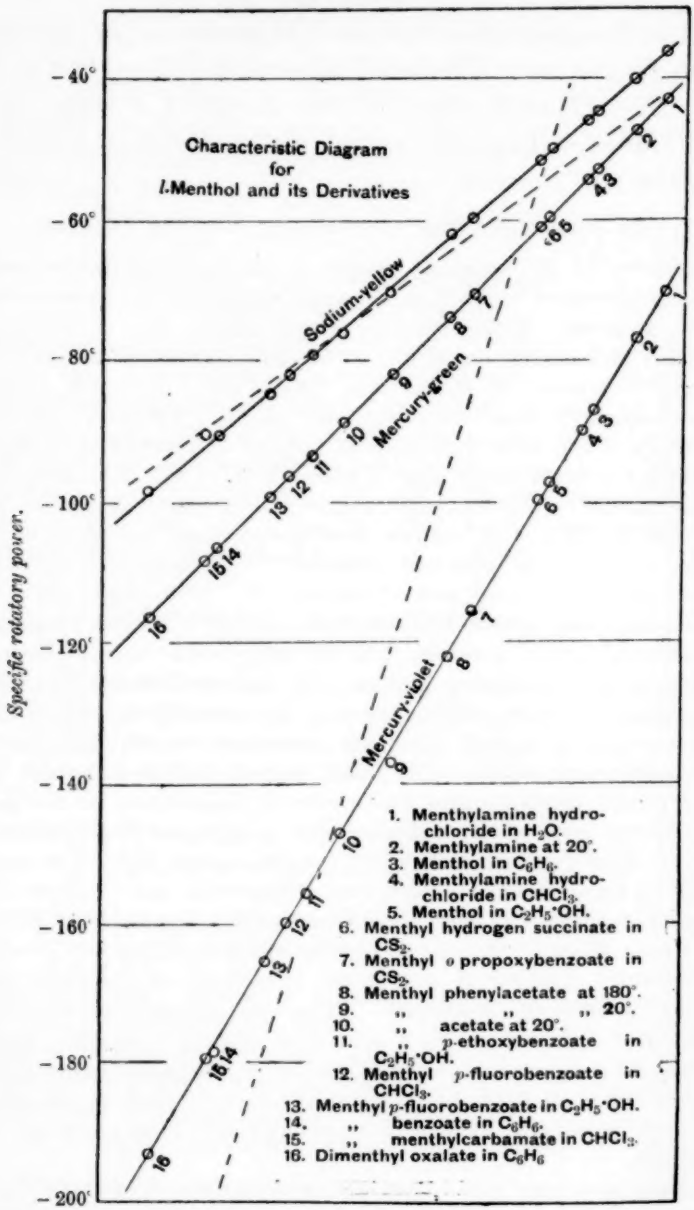
Thus homologous series of the *l*-menthyl esters of normal fatty acids (Tschugaev, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606), of the *l*-menthylamides of the same acids (Wallach and Binz, *Annalen*, 1893, **276**, 317), and of various derivatives of *l*-menthylcarbamic acid (Pickard and Littlebury, T., 1907, **91**, 300), have been shown to exhibit approximately a constant molecular rotatory power $[M]_D$. So regular have these values proved to be that some investigators (compare Hilditch, *inter alia*, T., 1909, **95**, 1570, and Frankland and O'Sullivan, T., 1912, **101**, 287) have based somewhat elaborate deductions on such a "series constant."

Although this question has already been briefly discussed (Pickard and Littlebury, *loc. cit.*), it appears desirable to attempt to discover further relations among the rotatory powers of these compounds. This is all the more important, as the comparison of the rotatory powers of unit mass, that is, of the molecular rotatory power, tends to give overwhelming importance to the factor due to the mass of the molecule with a corresponding obliteration of the effect due to the chemical constitution of the compounds.

From theoretical considerations, Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 388) have devised a method of plotting rotation values (known as "characteristic diagrams") which successfully explains at least some, if not all, of the cases of so-called anomalous dispersion, and the present authors have elaborated this method in a somewhat empirical manner, so that it has been applied in many instances in the more recent papers of this series of communications to the co-ordination of the specific rotatory powers of groups of compounds of allied chemical constitution.

It has now been found that one characteristic diagram will serve approximately to co-ordinate the specific rotatory powers of *l*-menthol, *l*-menthylamine, and many of their simpler derivatives. Thus in Fig. 1, after plotting the values for the mercury-green

FIG. 1.



The broken lines are copied from the lines for sodium-yellow and mercury-violet lights drawn in Fig. 3. For the sake of clearness only a few points have been placed in each figure.

light on a reference line of unit slope, it is found that the corresponding values for sodium-yellow and mercury-violet lights fall on two straight lines, of which the line for sodium-yellow intersects the reference line where [α] is zero, and that for mercury-violet where [α] is −3°. The compounds of which the specific rotatory powers have been found to conform to this generalisation are: *l*-menthol, the *l*-menthyl esters of acetic, oxalic, benzoic, *m*-toluic, phenylacetic, *p*-fluoro-, *m*-chloro-, *m*- and *p*-iodo-, 2-chloro-6-bromo-, *p*-methoxy-, *p*-ethoxy-, *o*-propoxy-, *p-iso*propoxy-, and *p*-allyloxybenzoic acids;* dimenthyl sulphite; *l*-menthyl hydrogen phthalate (in some solvents) and also its magnesium salt; *l*-menthylamine and its hydrochloride; dimenthylcarbamide; *l*-menthyl *l*-menthylcarbamate and several other amides and esters of *l*-menthylcarbamic acid containing the following radicles: ethyl, *n*-propyl, *n*-butyl, allyl, *m*- and *p*-tolyl, and *m*-4-xylenyl. Perhaps more striking than the list of compounds conforming to this generalisation is, however, the list of compounds of allied constitution with specific rotatory powers which do not lie on this characteristic diagram for *l*-menthyl derivatives. This includes the menthyl esters of *o*-iodo-, the mono- and di-nitro-benzoic and 2-methoxynaphthoic acids, 1- and 2-naphthyl esters and amides of *l*-menthylcarbamic acid, the sodium salt of *l*-menthyl hydrogen phthalate in aqueous solution, and (probably) compounds of the type of *m*-tolylmenthylcarbamide when dissolved in pyridine.

Many of the perplexing phenomena connected with the rotatory powers of carbon compounds have been ascribed to the occurrence of dynamic isomerism, and certainly the assumption of the existence of two isodynamic forms (with rotations of opposite sign and of different dispersive powers) of an esterified carboxylic group or of a substituted α-naphthyl group has allowed of a consistent explanation of the cases of the so-called "anomalous" dispersion described in this series of communications. In the cases of these menthyl compounds,† the departures from the generalisation given above (and in the majority of cases the compounds are those of which the molecular rotatory powers differ from the "series constant") can be accounted for in the following manner. The method of plotting rotation values known as "characteristic diagrams" allows for the presence in the otherwise homogeneous

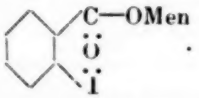
* The authors are very much indebted to Prof. J. B. Cohen, F.R.S., who has most generously placed at their disposal much costly and highly purified material prepared by him for an extended investigation of the menthyl esters of substituted benzoic acids of which a connected account has been given recently (T., 1914, **105**, 1892).

† None of which, however, exhibits under the available experimental conditions a so-called anomalous dispersion.

compound of two dynamic isomerides, but fails when more than two are present (see Part X, T., 1914, **105**, 2677, for instances of this already described). Thus in the cases of the menthyl compounds, the characteristic diagram for the menthyl group co-ordinates the specific rotatory powers of *l*-menthyl derivatives so long as these do not contain two dissimilar centres of possible dynamic isomerism. It can here be assumed that the amide group ·CO·NHR is as much a possible centre of dynamic isomerism as the ester group ·CO·OR has been shown in all probability to be. The presence of two similar centres of possible dynamic isomerism in a compound does not seem to prevent the co-ordination of its rotatory powers, but the evidence on this point is at present slender, being derived only from an examination of dimenthyl oxalate.

It may be observed from Fig. 2 that the yellow and green and violet lines all intersect very nearly where [α] is zero; as a result of this, any one of the three dispersion ratios violet/yellow, green-yellow, violet/green is very nearly constant for all compounds of which the rotation values fit on the diagram; the first and last ratios, however, will tend to be a function of the magnitude of the rotation, and decrease with its magnitude.* In the particular case, then, of these menthyl compounds, the approximate constancy of the dispersion ratio serves as a test of the normal character of the optical activity of the compound.†

The various exceptions to this co-ordination of the specific rotatory powers of the *l*-menthyl compounds may now be discussed. It will be observed that in the case of every exception the compound contains some modification of the carboxylic group, which itself is a possible centre of dynamic isomerism. Perhaps the most striking case is the menthyl ester of *o*-iodobenzoic acid, since it offers such a striking contrast to the corresponding *m*- and *p*-compounds. It is suggested that in the *o*-compound there is a second possible centre of dynamic isomerism, owing to the possibility of the formation of the complex



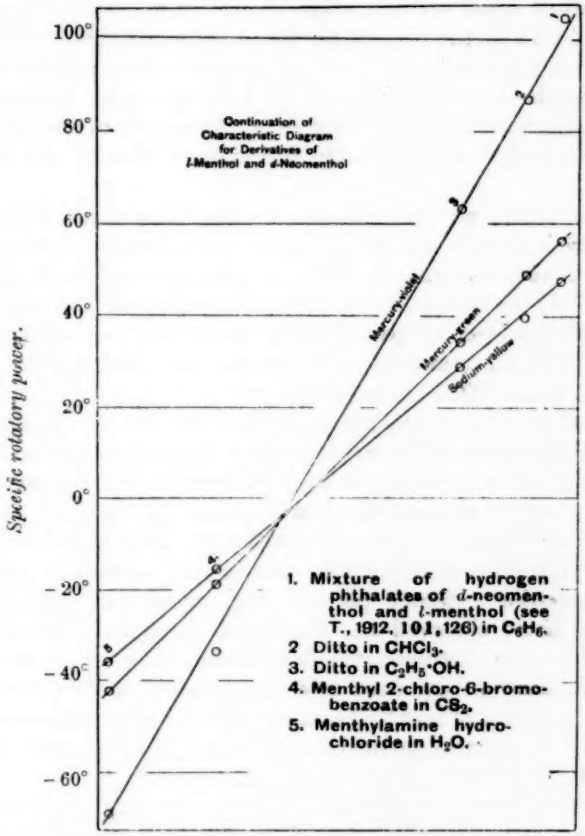
Somewhat in a similar manner it is suggested that the esters of

* Since the violet line does not intersect the others exactly where [α] is zero, slight discrepancies from this statement among the figures quoted in Tables I. and II. are probably due to errors in the "violet" readings, which are the less certain of the three and are often very much affected by any tinge of yellow colour in the substance.

† Compare, however, remarks on the use of dispersion ratios in Part X., *loc. cit.*

the nitro-substituted benzoic acids may contain either the grouping $\cdot N<^{O}_{O}$ or $\cdot N\ll^{O}_{O}$. An assumption of the existence of such isomerides, however intangible they may be, appears sufficient to explain the large effect of solution on these esters of nitrobenzoic acids. Here again the high rotatory powers of the *o*-nitrobenzoic

FIG. 2.



ester, and *inter alia* of the 2 : 6-dinitrobenzoic ester, may be directly due to the influence of the *o*-nitro-group on one of the isodynamic forms of the carboxylic group. Some confirmation of this view is afforded by the similar case of the 2-chloro-6-bromobenzoic ester, which when dissolved in carbon disulphide has an abnormally low rotatory power. This idea may be extended to give an alternative explanation of the successive variation of the

magnitude of rotatory powers of the menthyl esters of substituted benzoic acids put forward by Cohen (*loc. cit.*) to connect position isomerism and optical activity. Thus it may be suggested that the substituent lying nearest to the carboxylic group (not, as Cohen suggests, to the active group, although in the case of these esters the distance is measured from the same group) * produces the greatest effect, which, according to the nature of the substituent, may be either an increase or a decrease in the rotation value following upon an alteration in the proportion of the two isodynamic forms of the carboxylic group present in the compound. The consistent application of these ideas to so many compounds of varied type favours the underlying idea of much research in this field that the rotatory power of a derivative of (at least) a secondary alcohol is actually some function of that of the parent compound.

The abnormality of the dispersion ratios of the menthyl ester of 2-methoxynaphthoic acid and of the 1- and 2-naphthyl esters and amides of *l*-menthylcarbamic acid is readily explained by the assumption of the form of dynamic isomerism of the naphthyl group, which has been suggested as the explanation of the complex dispersion of the 1-naphthylalkylcarbinols described in Parts VI and IX (T., 1914, **105**, 1115, 2644).

The hypothesis can be readily applied to the case of the rotatory power of the sodium salt of *l*-menthyl hydrogen phthalate in aqueous solution, as it is easy to suggest more than two isodynamic forms of the active compound when dissolved in water.

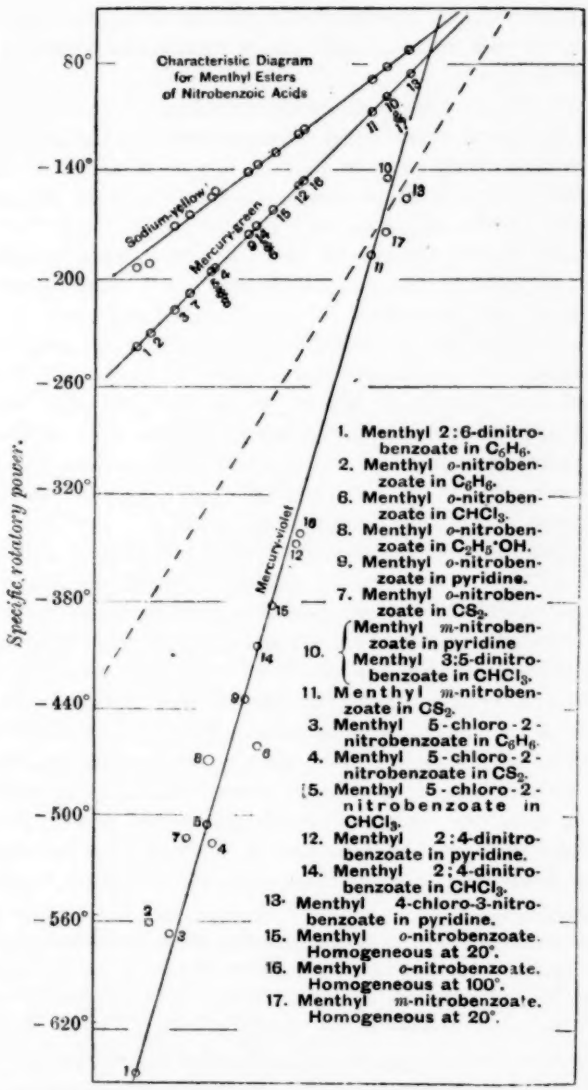
It has already been shown (Pickard and Littlebury, *loc. cit.*) that the aryl amides of *l*-menthylcarbamic acid exhibit in pyridine solution molecular rotatory powers $[M]_D$ which are considerably higher than those observed in chloroform solution. Probably all of these, like the *m*-tolylmenthylcarbamide, the only one now re-examined, have in pyridine solution dispersions different from that of the majority of menthyl compounds, and this difference may be caused by these aryl menthyl carbamides acting partly in the *iso*carbamide form when dissolved in this solvent.

Additional evidence in favour of the underlying hypothesis to explain these phenomena is afforded by the characteristic diagram (Fig. 3) which, drawn in the usual manner, serves to co-ordinate the rotations of the esters of mono- and di-nitrobenzoic acids observed under many conditions of temperature and solution. It will be seen that the diagram, like the dispersion ratios, differs greatly from that in Fig. 1.

* Analogous cases of the derivatives of optically active acids of simple constitution where the optically active group is the one to which the esterified carboxylic group is attached are under examination in this laboratory.

It has been shown by one of us and Littlebury (T., 1912, **101**, 109) that *l*-menthol and *d*-neomenthol correspond with *l*-menthone.

FIG. 3.



It is significant that the points, for example, Nos. 2, 6, 7, 8, which do not exactly fit on this diagram, refer to derivatives of *o*-nitrobenzoic acid. The diagram covers a much greater range (from [α] 60° to 660°) than the other diagrams. The broken line is the violet line copied from Fig. 1.

Thus, as the two menthols possess corresponding configurations, it is not surprising that the characteristic diagram for *l*-menthyl derivatives serves also to co-ordinate the rotatory powers of *d*-neomenthol and its derivatives (see Fig. 2).

When *l*-menthone is treated with alkalis or acids, it is partly converted into *iso*menthone, and yields a mixture which is generally dextrorotatory.

Since the rotatory powers of *l*-menthone and of various mixtures of ketones produced from it by inversion can be co-ordinated on one characteristic diagram (see Fig. 4), it may be inferred that the inversion takes place without any appreciable amount of racemisation (compare Tutin and Kipping, T., 1904, **85**, 66).

Further, the configuration of lævorotatory borneol corresponds with that of dextrorotatory *iso*borneol, since each gives when oxidised the same *l*-camphor (Pickard and Littlebury, T., 1907, **91**, 1973). As may be therefore expected, one diagram (see Fig. 5) serves to co-ordinate the rotatory powers of *l*-borneol, *d*-*iso*borneol, and their derivatives, whilst the irregular behaviour of the hydrogen phthalates of the borneols (like that of the corresponding menthyl compound under some conditions) suggests that the two groups ·CO·OR and ·CO·OH can function as two dissimilar centres of possible dynamic isomerism.

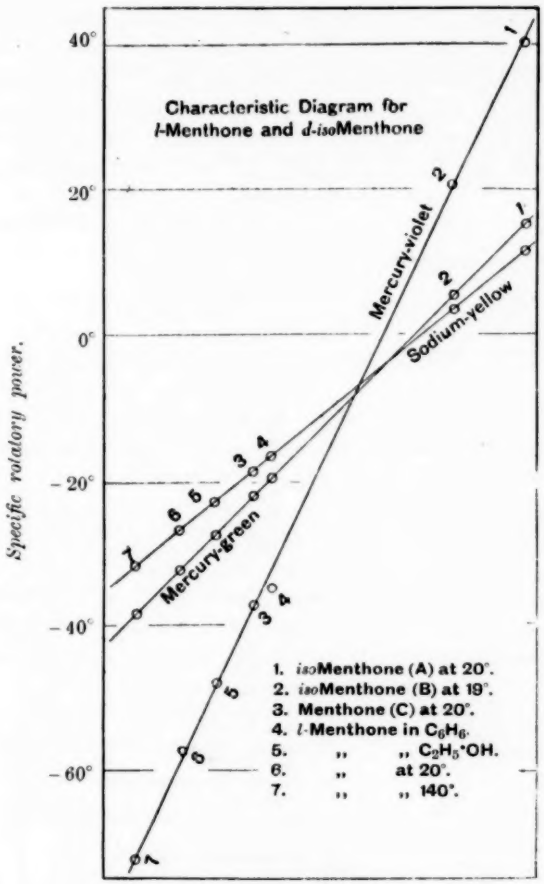
It may therefore be suggested that the extension of this method will result in the recognition of many of the more elusive forms of isomerism which have been postulated in so many instances to explain some of the more obscure reactions in organic chemistry.

The great majority of the observed rotations recorded in this paper conform approximately to the Drude equation with one term, $\alpha = k/\lambda^2 - \lambda^2_0$. That the dispersive power of these compounds is found thus to be simple is not perhaps very surprising, for there appear to be other instances known where a mixture of isodynamic forms of a substance exhibits simple dispersive power; thus, for example, the solutions of fructose at various concentrations described by Armstrong and Walker (*loc. cit.*) exhibit simple rotatory dispersion.

However, some of our observed rotations do not conform to the Drude equation with one term, and the following list of these substances which in the homogeneous state or in solution exhibits complex dispersive power shows many analogies with the results previously recorded: solutions of the menthyl esters of *o*-nitro-, 2:4- and 3:5-dinitrobenzoic acids in benzene, pyridine, chloroform, and alcohol; solutions of the hydrogen phthalates and of the menthyl ester of 2-methoxynaphthoic acid. Further, the following compounds at high temperatures exhibit complex

dispersive power: the menthyl esters of acetic, phenylacetic, *p*-methoxy- and *o*-nitro-benzoic acids, *l*-bornyl acetate, *l*-menthyl-

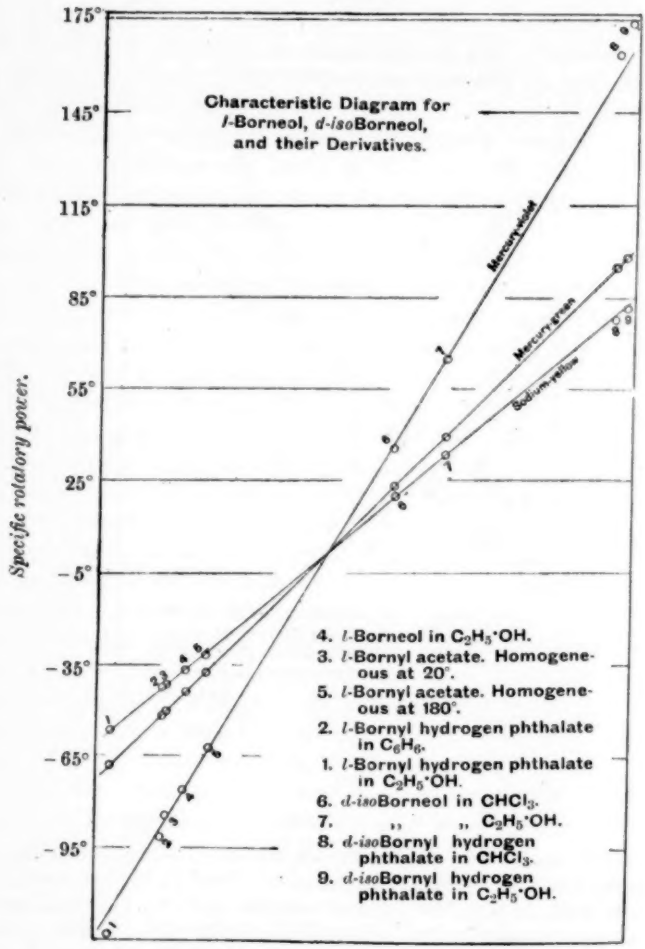
FIG. 4.



Points 6 and 7 refer to the rotations of a sample of pure *l*-menthone investigated in the homogeneous state in a glass polarimeter tube. The sample after heating to 180° was found when cold to have a lower rotation and was doubtless partly inverted owing to enolisation induced by the alkali of the glass. Points 3 and 5 refer to *l*-menthone dissolved in benzene and alcohol respectively. Point 4 refers to the rotatory power of a partially inverted *l*-menthone (*C*) which had been prepared by heating *l*-menthone for a short time with a solution of sodium hydroxide. The samples of *iso*menthone (*A* and *B*) to which points 1 and 2 refer were obtained as follows: *l*-menthone was partly reduced by the Sabatier process and the resulting menthols removed by treatment of one preparation with benzoyl chloride and of a second preparation with phthalic anhydride. From the residues of these two preparations were obtained the two samples (marked *A* and *B*) of *iso*menthone.

amine, and *l*-menthone (having then undergone some inversion). It seems probable that the rotations of a substance displaying dynamic isomerism will conform to the law of simple dispersion if the two isodynamic forms have the same dispersive power,

FIG. 5.



in which case the lines of its characteristic diagram will intersect where $[\alpha]$ is zero.

EXPERIMENTAL.

With two exceptions, all the compounds, which have now been submitted to an extended re-examination in the polarimeter, have

been described in the investigations of Cohen and his pupils (*loc. cit.*) and in those of one of us and Littlebury (*loc. cit.*).

Di-l-menthyl sulphite, $(C_{10}H_{19}O)_2SO$, is readily obtained when equivalent amounts of thionyl chloride and *l*-menthol, each diluted with much light petroleum, are slowly mixed and allowed to react at a temperature not exceeding 6°. The ester is separated from unchanged menthol by fractional distillation. It boils at 210°/9 mm., and solidifies to a white mass, which crystallises readily from dilute alcohol in colourless, glistening needles, melting at 52°. It was analysed by titration with iodine of the sulphurous acid formed on hydrolysis.

Found, S = 8·66.

$C_{20}H_{38}O_3S$ requires S = 8·94 per cent.

Magnesium l-Menthyl Phthalate.—This salt is precipitated on mixing solutions of magnesium chloride and sodium *l*-menthyl phthalate, and crystallises very readily from dilute alcohol in glistening flakes.

The menthyl esters on loan from Prof. Cohen were in the majority of cases used in the condition as received from him. The rotations observed for sodium light were generally in close agreement with his results. Some of the esters were redistilled at a low pressure, and the very slight diminution of rotatory power which resulted was not taken into account. The general experimental conditions for the determination of density and of rotatory power (both in solution and in the homogeneous state) were the same as previously described in this series of investigations.

Table I.

Rotations of Various Compounds in the Homogeneous State at Different Temperatures.*

l-*Menthol*.

Temp.	D'_4.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg^{violet}}{green}$
20°	0·9007	−48·96°	−51·39°	−57·90°	−96·61°	−76·19°	−80·13°	−90·33°	−150·7°	1·978	1·185	1·668
40	0·8848	49·55	52·10	58·80	97·61	77·29	81·27	91·73	152·3	1·970	1·187	1·660
60	0·8690	50·02	52·34	59·30	98·15	78·03	81·66	92·51	153·1	1·962	1·185	1·655
80	0·8534	49·97	52·06	58·95	97·97	77·94	81·21	91·96	152·9	1·961	1·180	1·662
100	0·8379	49·48	51·53	58·21	97·03	77·18	80·39	90·80	151·4	1·961	1·177	1·666
120	0·8223	48·78	50·94	57·48	95·82	76·10	79·45	89·66	149·5	1·964	1·179	1·667
140	0·8070	48·15	50·34	56·78	94·66	75·11	78·52	88·57	147·7	1·966	1·180	1·667
160	0·7917	47·58	49·76	56·14	93·46	74·23	77·62	87·58	145·7	1·963	1·180	1·664
180	0·7760	47·09	49·09	55·59	92·04	73·45	76·58	86·72	143·5	1·954	1·180	1·659

l-*Menthyl Acetate*.

20°	0·9264	−79·41°	−83·01°	−94·12°	−156·1°	−157·2°	−164·4°	−186·4°	−309·1°	1·966	1·185	1·659
40	0·9090	79·20	82·73	93·58	155·7	156·8	163·9	185·8	308·2	1·965	1·184	1·659
60	0·8916	78·98	82·47	93·50	155·2	156·4	163·3	185·1	307·3	1·965	1·184	1·660
80	0·8733	78·89	82·31	93·28	155·1	156·3	163·4	184·7	307·0	1·966	1·182	1·662
100	0·8570	78·57	81·98	92·90	154·4	155·6	162·4	184·0	305·7	1·965	1·182	1·662
120	0·8400	78·34	81·74	92·64	153·9	155·2	161·8	183·4	304·8	1·965	1·182	1·662
140	0·8232	78·11	81·51	92·34	153·4	154·6	161·4	182·8	303·8	1·964	1·180	1·661
160	0·8061	77·89	81·26	92·04	152·9	154·3	160·9	182·3	302·8	1·963	1·181	1·661
180	0·7892	77·62	81·00	91·70	152·4	153·7	160·4	181·6	301·8	1·963	1·181	1·662

* All rotations recorded in this paper are negative unless otherwise stated. The values in Table I. are deduced from data recorded on page 60 *et seq.*

TABLE I. (*continued*).

l-*Dimenthyl Oxalate.*

Temp.	D_4^t.	$[\alpha]_D$.	$[\alpha]_{yc}$.	$[\alpha]_{gr}$.	$[\alpha]_{vl}$.	$[M]_D$.	$[M]_{yc}$.	$[M]_{gr}$.	$[M]_{vl}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	$\frac{Hg_{violet}}{Hg_{green}}$.
20°	0·9833	−93·46°	−97·61°	−110·4°	−182·0°	−342·1°	−357·3°	−404·0°	−666·3°	1·948	1·181	1·649
40	0·9676	93·28	97·40	110·1	181·9	341·4	356·6	403·1	666·6	1·949	1·180	1·651
60	0·9516	93·11	97·21	109·9	181·5	340·8	355·8	402·3	664·4	1·949	1·180	1·651
80	0·9358	92·87	96·99	109·6	181·0	339·9	355·0	401·0	662·6	1·949	1·180	1·653
100	0·9200	92·64	96·61	109·2	180·3	339·0	353·6	399·5	660·0	1·946	1·179	1·652
120	0·9042	92·10	96·10	108·8	179·6	337·1	351·8	398·2	657·4	1·950	1·181	1·652
140	0·8885	91·68	95·43	108·1	178·9	335·5	349·2	395·7	655·0	1·953	1·180	1·655
160	0·8731	91·11	94·77	107·4	178·0	333·5	346·9	393·2	651·5	1·954	1·179	1·657
180	0·8574	90·38	94·04	106·6	177·0	330·9	344·2	390·1	647·7	1·958	1·179	1·661
						l-*Menthyl Phenylacetate.*						
20°	1·0020	−68·06°	−71·34°	−81·14°	−137·4°	−186·5°	−195·4°	−222·3°	−376·5°	2·018	1·192	1·693
40	0·9867	67·41	70·44	80·09	135·6	184·7	193·1	219·5	371·6	2·012	1·189	1·692
60	0·9711	66·65	69·56	79·07	133·8	182·4	190·6	216·7	366·5	2·009	1·188	1·692
80	0·9557	65·66	68·58	77·87	131·9	179·9	187·9	213·4	361·3	2·008	1·186	1·693
100	0·9402	64·74	67·54	76·72	130·0	177·4	185·1	210·2	356·2	2·003	1·185	1·694
120	0·9246	63·89	66·62	75·80	128·1	175·1	182·6	207·7	350·9	1·996	1·187	1·690
140	0·9092	62·95	65·67	74·87	126·1	172·5	180·0	205·1	345·4	2·002	1·190	1·684
160	0·8936	62·07	64·92	73·91	123·9	170·1	178·3	202·5	339·7	1·997	1·191	1·677
180	0·8779	61·55	64·40	73·02	121·9	168·7	176·5	200·0	333·9	1·980	1·187	1·669

TABLE I. (*continued*).

Temp.	D^t_4.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	Hg^{violet}_{green}.
l-*Menthyl* p-*Methoxybenzoate*.												
20°	1·0360	−86·22°	−90·12°	−102· 6°	−174·7°	−250·0°	−261·3°	−297·5°	−505·7°	2·026	1·162	1·703
40	0·9964	87·42	90·38	103· 6	175·7	252·9	262·1	300·6	509·5	2·013	1·188	1·694
60	0·9897	85·39	89·43	101· 4	170·1	247·7	258·7	293·9	493·3	1·992	1·187	1·678
80	0·9834	83·52	87·44	99·04	167·2	242·2	253·0	287·2	484·8	2·001	1·186	1·688
100	0·9767	81·64	85·31	96·70	163·2	236·8	247·4	280·4	473·3	2·004	1·184	1·689
120	0·9698	79·82	83·45	94·64	159·1	231·5	241·9	274·5	461·4	1·993	1·186	1·681
140	0·9636	78·03	81·68	92·47	155·4	226·3	236·9	268·1	450·7	1·992	1·185	1·681
160	0·9568	76·28	79·79	90·28	151·9	221·2	231·4	261·8	440·5	1·991	1·184	1·682
180	0·9498	74·87	78·00	88·35	148·7	217·1	226·2	256·3	431·1	1·986	1·180	1·682
l-*Menthyl* o-*Iodobenzoate*.												
19°	1·375°	−61·35°	−64·30°	−73·57°	−130·8°	−236·8°	−248·2°	−284·0°	−504·8°	2·131	1·199	1·777
70·5	1·330	61·02	63·90	73·16	130·4	235·6	246·7	282·4	503·2	2·136	1·199	1·781
l-*Menthyl* m-*Iodobenzoate*.												
19°	1·376	−61·22°	−63·90°	−72·67°	−121·8°	−236·3°	−246·6°	−280·5°	−470·2°	1·989	1·187	1·676
l-*Menthyl* p-*Iodobenzoate*.												
19°	1·312	−63·63°	−66·50°	−75·30°	−126·7°	−245·6°	−256·7°	−290·7°	−488·9°	1·991	1·184	1·682
l-*Menthyl* o-*Nitrobenzoate*.												
20°	1·1140	−128·7°	−136·4°	−161·3°	−381·9°	−392·4°	−425·8°	−492·0°	−1164·7°	2·968	1·254	2·367
40	1·0974	126·1	133·8	157·9	372·7	384·7	408·0	481·5	1136·7	2·955	1·252	2·361
60	1·0810	123·6	131·0	154·4	362·9	377·0	399·5	470·8	1106·3	2·935	1·249	2·350
80	1·0645	121·2	128·1	151·0	352·4	369·6	390·8	460·4	1074·8	2·908	1·246	2·334
100	1·0480	119·0	125·2	147·6	341·8	362·9	381·8	450·2	1042·5	2·873	1·241	2·316
120	1·0320	117·3	123·4	145·5	—	357·9	376·5	443·9	—	—	1·240	—
140	1·0154	115·9	122·1	143·9	—	353·5	372·5	438·8	—	—	1·241	—
160	0·9994	114·4	120·7	142·1	—	349·0	368·1	433·4	—	—	1·242	—
180	0·9830	112·9	119·3	140·2	—	344·4	363·8	427·6	—	—	1·242	—

TABLE I. (*continued*).

Temp.	D^t_4.	$[\alpha]_{D.}$	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_{D.}$	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg^{violet}}{green}$
l-*Menthyl* m-*Nitrobenzoate*.												
20°	1·1173	−82·52°	−86·30°	−98·44°	−173·6°	−251·7°	−263·2°	−300·2°	−529·4°	2·108	1·193	1·763
40	1·0990	82·14	85·93	97·90	—	250·5	262·1	298·6	—	—	1·192	—
60	1·0818	81·70	85·43	97·25	—	249·2	260·6	296·6	—	—	1·190	—
80	1·0646	81·06	84·76	96·44	—	247·2	258·5	294·1	—	—	1·190	—
100	1·0473	80·39	84·00	95·72	—	245·2	256·2	292·0	—	—	1·191	—
120	1·0302	79·68	83·28	94·95	—	243·0	254·0	289·6	—	—	1·192	—
140	1·0131	78·93	82·59	94·18	—	240·7	251·9	287·2	—	—	1·193	—
160	0·9959	78·42	82·27	93·66	—	239·1	250·9	285·7	—	—	1·194	—
180	0·9787	78·70	82·56	93·65	—	240·1	251·2	285·7	—	—	1·190	—
l-*Menthyl* p-*Nitrobenzoate*.												
20°	1·120	−70·99°	−73·98°	−83·33°	—	−216·5°	−225·6°	−254·2°	—	—	1·174	—
40	1·100	70·86	73·91	83·45	—	216·1	225·4	254·5	—	—	1·178	—
60	1·080	70·73	73·72	83·28	—	215·7	224·9	254·0	—	—	1·177	—
80	1·060	70·60	73·57	83·12	—	215·3	224·4	253·5	—	—	1·177	—
100	1·041	70·34	73·40	82·83	—	211·7	223·9	252·6	—	—	1·177	—
120	1·022	70·18	73·16	82·59	—	214·1	223·1	251·9	—	—	1·177	—
140	1·003	69·98	73·05	82·47	—	213·4	222·8	251·6	—	—	1·176	—
160	0·9984	69·08	71·86	81·64	—	210·7	219·2	249·0	—	—	1·181	—
180	0·9967	67·33	70·44	79·50	—	205·3	214·8	242·8	—	—	1·182	—
l-*Menthyl* p-*Allyloxybenzoate*.												
20°	1·027	−79·76°	−83·55°	−94·14°	−164·60°	−252·1°	−264·0°	−297·5°	−508·3°	2·027	1·180	1·709

TABLE I. (*continued*).

l-*Menthylamine*.

Temp.	D'_4.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	$Hg\frac{violet}{green}$.
20°	0·8560	−39·97°	−41·63°	−47·04°	−76·40°	−61·95°	−64·52°	−72·91°	−118·4°	1·911	1·177	1·624
40	0·8402	40·81	42·51	48·07	78·03	63·24	65·89	74·50	121·0	1·913	1·179	1·624
60	0·8244	41·52	43·24	48·88	79·47	64·34	67·02	75·75	123·1	1·914	1·177	1·626
80	0·8088	42·14	43·96	49·58	80·85	65·31	68·14	76·85	125·3	1·919	1·177	1·631
100	0·7933	42·76	44·62	50·27	82·22	66·27	69·15	77·91	127·5	1·923	1·176	1·636
120	0·7775	43·40	45·21	51·01	83·75	67·26	70·06	79·07	129·8	1·930	1·176	1·642
140	0·7620	44·01	45·75	51·69	85·09	68·22	70·91	80·11	131·9	1·933	1·174	1·646
160	0·7463	44·61	46·20	52·32	86·52	69·13	71·61	81·10	134·1	1·939	1·173	1·654
180	0·7310	45·02	46·69	52·81	87·78	69·77	72·36	81·85	136·0	1·950	1·173	1·663
						l-*Menthone*.*						
20°	0·8977	−26·74°	−27·84°	−32·07°	−57·15°	−41·17°	−42·87°	−49·39°	−88·00°	2·137	1·199	1·781
40	0·8732	27·65	28·89	33·29	59·92	42·57	44·49	51·24	92·28	2·168	1·204	1·801
60	0·8590	28·36	29·79	34·38	62·61	43·68	45·76	52·93	96·40	2·207	1·212	1·822
80	0·8446	29·32	30·67	35·48	65·55	45·15	47·23	54·64	100·9	2·236	1·210	1·848
100	0·8303	30·43	31·77	36·82	68·84	46·86	48·93	56·70	106·0	2·262	1·210	1·865
120	0·8159	31·41	32·88	38·18	71·83	48·37	50·63	58·79	110·6	2·288	1·215	1·881
140	0·8020	31·63	33·13	38·63	72·13	48·71	51·02	59·48	111·1	2·280	1·221	1·863
160	0·7876	31·48	33·06	38·43	71·48	48·48	50·90	59·19	110·1	2·271	1·221	1·860
180	0·7735	31·77	33·09	38·37	71·52	48·91	50·95	59·09	110·1	2·252	1·208	1·864

* See footnote to Fig. 4, page 43.

TABLE I. (*continued*).

Temp.	D'_4.		$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_{D.}$	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	$\frac{Hg_{violet}}{Hg_{green}}$.
					*Menthone A.**							
19°	0·8983	+3·74°	+4·25°	+5·61°	+20·55°	+5·76°	+6·55°	+8·64°	+31·65°	5·494	1·500	3·663
					*Menthone B.**							
20°	0·8977	+11·56°	+12·32°	+15·22°	+40·10°	+17·80°	+18·97°	+23·43°	+61·76°	3·468	1·316	2·636
					*Menthone C.**							
20°	0·8977	−18·74°	−19·49°	−22·12°	−37·09°	−28·85°	−30·02°	−34·06°	−55·82°	1·935	1·180	1·639
					l-*Bornyl Acetate.*							
20°	0·9868	−42·43°	−44·16°	−50·18°	−84·33°	−83·18°	−86·56°	−98·35°	−163·5°	1·987	1·182	1·681
40	0·9691	40·75	42·49	48·19	80·98	79·87	83·30	94·48	158·8	1·987	1·182	1·681
60	0·9523	39·06	40·71	46·18	77·49	76·58	79·82	90·53	151·9	1·979	1·182	1·678
80	0·9334	37·64	39·22	44·52	74·56	73·79	76·90	87·28	146·2	1·981	1·182	1·674
100	0·9157	36·44	38·08	43·16	72·40	71·44	74·64	84·61	141·9	1·986	1·184	1·677
120	0·8977	35·22	36·84	41·80	70·04	69·02	72·21	81·94	137·3	1·989	1·187	1·676
140	0·8797	34·00	35·58	40·46	67·79	66·65	69·74	79·30	132·9	1·994	1·190	1·676
160	0·8618	33·04	34·47	39·09	65·55	64·76	67·57	76·63	128·5	1·985	1·183	1·677
180	0·8437	32·30	33·55	37·67	63·43	63·33	65·75	73·84	124·3	1·963	1·166	1·684

* See footnote to Fig. 4, page 43.

Table II.

Determinations of Rotatory Power in (approx.) 5 per cent. Solutions.

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_D$.	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_D$.	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet.}}{Na_{yellow}}$	$\frac{Hg_{green.}}{Na_{yellow}}$	$\frac{Hg_{violet.}}{Hg_{green}}$
l-*Menthol.*																	
C_2H_5OH ...	20	1·0328	−5·11°	−5·35°	−6·11°	−10·03°	−49·46°	−51·80°	−59·14°	−97·09°	−76·77°	−80·28°	−91·66°	−150·5°	1·963	1·196	1·642
CS_2	20	1·0571	4·97	5·19	5·88	9·85	47·03	49·11	55·64	93·19	72·90	76·12	86·24	144·4	1·962	1·183	1·675
C_6H_6.....	22	1·1064	5·55	5·79	6·57	10·80	44·60	46·52	52·78	86·78	69·11	72·11	81·83	134·5	1·945	1·184	1·644
l-*Menthyl Acetate.*																	
CS_2	20	1·0360	7·98	8·42	9·45	15·60	77·01	81·27	91·20	150·58	151·7	160·1	179·7	296·6	1·954	1·184	1·651
C_2H_5OH...	20	1·1582	9·87	10·31	11·69	19·40	85·23	89·02	100·93	167·50	167·9	175·4	198·9	330·1	1·965	1·184	1·660
l-*Dimenthyl Oxalate.*																	
C_2H_5OH...	20	1·0556	10·33	10·75	12·20	20·28	97·86	101·84	115·57	192·12	358·1	372·7	423·0	703·2	1·963	1·181	1·662
CS_2	20	0·9589	7·87	8·23	9·27	15·15	82·08	85·82	96·68	157·99	300·4	314·2	353·8	578·3	1·925	1·178	1·634
C_6H_6.....	20	0·9849	9·67	10·10	11·44	18·99	98·18	102·55	116·25	192·81	359·4	375·3	425·1	705·7	1·964	1·183	1·660
C_5H_5N	22	0·9499	9·79	10·18	11·58	19·21	93·69	97·43	110·83	183·84	342·9	356·6	405·6	672·9	1·962	1·183	1·659
l-*Menthyl Benzoate.*																	
C_6H_6.....	10	1·0403	4·70	4·89	5·55	9·29	90·38	96·01	106·70	178·60	234·1	248·6	276·5	462·7	1·976	1·181	1·674
$CHCl_3$	20	1·0368	8·98	9·40	10·60	17·60	86·61	90·66	102·24	169·75	224·3	234·8	264·8	439·6	1·960	1·180	1·661
l-*Menthyl* m-*Toluate.*																	
C_6H_6.....	22	1·0062	9·79	10·20	11·62	19·55	88·47	92·17	104·99	176·63	242·4	252·7	287·7	484·1	1·996	1·187	1·682
l-*Menthyl Phenylacetate.*																	
C_6H_6.....	10	1·0152	3·27	3·42	3·87	6·52	64·43	67·39	76·26	128·45	176·0	184·7	208·9	352·1	1·994	1·184	1·685

TABLE II. (*continued*).

Determinations of Rotatory Power in (approx.) 5 *per cent. Solutions.*

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_D$.	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_D$.	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet.}}{Na_{yellow}}$	$\frac{Hg_{green.}}{Na_{yellow}}$	$\frac{Hg_{violet.}}{Hg_{green}}$
l-Menthyl p-*Fluorobenzoate.*																	
C_5H_5N	20	1·0624	8·65°	9·02°	10·21°	17·06°	81·45°	84·94°	96·14°	160·58°	226·4°	237·2°	267·3°	446·5°	1·972	1·180	1·670
$CHCl_3$	20	0·9695	7·92	8·28	9·36	15·50	81·70	85·41	96·56	159·87	227·1	237·4	268·4	445·4	1·957	1·182	1·656
$C_2H_5{\cdot}OH$...	22	0·9477	8·80	9·14	10·36	17·26	84·37	87·62	99·33	165·57	234·5	234·5	276·2	459·9	1·961	1·177	1·665
CS_2	10	0·9108	4·11	4·25	4·86	8·26	90·24	93·33	106·72	181·38	250·8	259·4	296·6	504·2	2·010	1·182	1·700
C_6H_6.....	20	0·9654	8·38	8·76	9·93	16·71	86·80	90·74	102·86	173·09	241·3	252·3	285·9	481·1	1·995	1·185	1·683
l-Menthyl m-*Chlorobenzoate.*																	
CS_2	20	1·1350	9·67	10·11	11·50	19·50	85·19	89·07	100·13	171·80	250·9	262·3	298·4	506·0	2·017	1·189	1·696
l-Menthyl m-*Iodobenzoate.*																	
C_5H_5N	22	1·0574	6·79	7·09	8·02	13·40	58·38	62·37	68·96	115·20	225·4	240·7	266·2	444·7	1·973	1·181	1·670
CS_2	10	1·2382	3·96	4·10	4·63	7·91	63·97	66·24	74·80	127·77	246·9	255·7	288·7	[493·3	1·997	1·169	1·708
l-Menthyl p-*Iodobenzoate.*																	
$CH_3{\cdot}CO_2Et$	22	1·2113	7·64	7·98	9·02	14·87	57·36	59·91	67·72	111·61	221·4	231·3	261·4	430·9	1·946	1·180	1·648
C_6H_6.....	10	1·1422	3·98	4·12	4·69	7·98	69·69	72·14	82·13	139·73	269·0	278·5	317·1	539·4	2·004	1·179	1·701
l-Menthyl 2-*Chloro*-6-*bromobenzoate.*																	
CS_2 ?.....	10	0·9559	0·75	0·80	0·91	1·63	15·69	16·74	19·04	33·88	58·7	62·7	71·3	127·0	2·173	1·214	1·792
l-Menthyl p-*Ethoxybenzoate.*																	
$C_2H_5{\cdot}OH$ ...	20	0·9432	7·09	7·35	8·38	13·85	76·15	77·93	88·84	146·84	228·5	236·9	270·1	446·5	1·954	1·182	1·653

TABLE II. (*continued*).

Determinations of Rotatory Power in (approx.) 5 per cent. Solutions.

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	α_{ye}.	α_{gr}.	α_{vi}.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\sigma]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg_{violet}}{Hg_{green}}$
l-*Menthyl* o-*Propoxybenzoate*.																	
CS_2	20	0·9794	5·86°	6·11°	6·89°	11·30°	59·82°	62·37°	70·34°	115·45°	190·2°	198·4°	223·7°	366·8°	1·929	1·176	1·640
l-*Menthyl* p-iso*Propoxybenzoate*.																	
C_6H_6.....	20	0·9578	7·62	7·97	9·06	15·46	79·56	83·22	94·58	161·41	253·0	264·6	300·7	513·3	2·029	1·189	1·706
***Di*-l-*menthyl Sulphite*.**																	
$C_2H_5{\cdot}OH$...	20	0·9846	7·76	8·05	9·18	15·35	78·81	81·75	93·22	155·90	282·1	292·7	333·7	558·1	1·978	1·182	1·672
l-*Menthyl Hydrogen Phthalate*.																	
$CHCl_3$	20	0·9942	9·32	9·73	11·25	20·40	93·74	97·86	113·15	205·19	284·0	296·5	342·8	[621·7	2·199	1·207	1·813
***Magnesium* l-*Menthyl Phthalate*.**																	
$C_2H_5{\cdot}OH$...	20	0·7531	4·16	4·34	4·90	8·20	55·23	57·62	65·06	108·88	180·0	187·8	212·0	354·9	1·972	1·179	1·673
l-*Menthyl Hydrogen Succinate*.																	
C_6H_6.....	22	1·0164	6·65	6·96	7·88	13·00	59·43	62·24	70·47	116·27	152·2	159·3	180·4	297·7	1·956	1·186	1·650
$CHCl_3$	22	1·0190	7·36	7·68	8·75	14·45	65·65	68·50	78·05	128·91	168·1	175·4	199·7	330·0	1·963	1·189	1·652
l-*Menthyl Phenylcarbamate*.																	
$CHCl_3$	20	0·9920	7·63	7·94	9·11	15·20	76·91	80·04	91·83	153·22	211·4	220·4	252·4	421·4	1·992	1·194	1·668

TABLE II. (*continued*).

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	α_{ye}.	α_{gr}.	α_{vi}.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg_{violet}}{Hg_{green}}$
l-*Menthylamine Hydrochloride*.																	
H_2O	22	1·0243	4·09°	4·22°	4·80°	7·87°	36·29°	37·45°	42·60°	69·85°	43·38°	44·76°	50·91°	83·49°	1·924	1·173	1·640
$CHCl_3$	20	0·9974	4·56	4·75	5·40	8·96	45·72	49·86	54·14	89·82	87·54	95·48	103·6	172·0	1·964	1·184	1·659
***Di*-l-*menthylcarbamide*.**																	
$CHCl_3$	20	0·9368	8·55	8·95	10·12	16·98	91·26	95·53	108·02	181·25	306·6	320·9	362·9	609·0	1·986	1·184	1·678
***Ethyl* l-*Menthylcarbamate*.**																	
$CHCl_3$	20	0·7881	5·40	5·62	6·43	10·79	68·52	71·31	81·58	137·0	155·5	161·8	185·2	391·3	1·998	1·191	1·678
n-*Propyl*-l-*menthylcarbamide*.																	
$CHCl_3$	20	0·5557	3·72	3·86	4·40	7·40	66·94	69·47	79·20	133·17	159·3	165·4	188·5	317·0	1·989	1·183	1·682
n-*Butyl* l-*Menthylcarbamate*.																	
$CHCl_3$	22	0·8854	6·25	6·50	7·42	12·54	64·18	66·74	76·19	128·76	163·6	170·2	194·3	328·3	2·006	1·186	1·690
***Allyl*-l-*menthylcarbamate*.**																	
$C_2H_5{\cdot}OH$...	20	0·8705	5·86	6·10	6·95	11·75	67·33	70·08	79·86	135·98	160·9	167·5	190·8	322·7	2·005	1·186	1·690
p-*Tolyl* l-*Menthylcarbamate*.																	
$CHCl_3$	20	0·3930	2·22	2·30	2·63	4·44	56·49	58·52	66·92	112·98	163·2	169·2	193·4	326·5	2·000	1·185	1·689

TABLE II. (*continued*).

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_D$.	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_D$.	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg^{violet}}{green}$
m-*Tolyl* l-*Menthylcarbamate*.																	
$CHCl_3$	10	0·5878	1·65°	1·74°	1·96°	3·39°	56·14°	59·20°	66·70°	115·35°	162·3°	171·1°	192·8°	333·4°	2·054	1·181	1·730
m-4-*Xylenyl* l-*Menthylcarbamate*.																	
$CHCl_3$	22	0·7707	4·57	4·72	5·39	9·16	53·91	55·67	63·57	108·05	163·3	168·7	192·6	327·3	2·004	1·180	1·699
l-*Menthyl* l-*Menthylcarbamate*.																	
$CHCl_3$	20	0·9497	8·55	8·89	10·10	16·93	90·02	93·60	106·34	178·26	303·3	315·4	358·4	600·7	1·980	1·181	1·676
l-*Menthyl* o-*Iodobenzoate*.																	
CS_2	22	1·0348	6·67	7·03	8·01	14·17	58·59	61·76	70·34	124·49	226·1	238·4	271·6	480·5	2·124	1·200	1·769
l-*Menthyl* o-*Nitrobenzoate*.																	
C_5H_5N	20	1·0143	14·09	14·90	17·75	43·17	138·91	146·90	175·00	435·52	422·7	448·0	533·8	1299·1	3·064	1·260	2·432
$CHCl_3$	22	1·0302	17·38	18·36	21·79	52·35	154·01	162·01	170·67	461·97	466·8	494·2	520·5	1409·0	3·012	1·113	2·707
$C_2H_5{\cdot}OH$.	10	0·9848	7·72	8·15	9·63	22·99	156·78	165·52	195·57	466·90	478·0	504·8	596·4	1424·0	2·979	1·247	2·388
CS_2	10	1·1145	9·07	9·60	11·45	28·60	162·76	172·27	208·08	513·34	496·5	525·5	626·8	1565·7	3·154	1·263	2·498
C_6H_6	20	0·8399	15·32	16·25	19·34	47·05	182·40	193·47	230·27	560·18	556·3	590·1	702·3	1708·6	3·071	1·262	2·433
l-*Menthyl* m-*Nitrobenzoate*.																	
C_5H_5N	20	1·1743	9·60	10·06	11·48	20·36	81·75	85·67	97·76	173·34	249·3	261·3	298·2	528·8	2·121	1·196	1·774
CS_2	20	1·4219	12·65	13·26	15·14	26·46	88·97	92·83	106·48	186·09	271·4	284·4	324·8	567·5	2·092	1·197	1·748

TABLE II. (*continued*).

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_{D.}$	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_{D.}$	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$	$\frac{Hg_{green}}{Na_{yellow}}$	$\frac{Hg_{violet}}{Hg_{green}}$
l-*Menthyl* 5-*Chloro*-2-*nitrobenzoate*.																	
CS_2	20	0·9048	13·71°	14·59°	17·55°	46·70°	151·53°	161·25°	193·97°	516·14°	514·2°	547·3°	658·5°	1752·0°	3·406	1·280	2·661
C_6H_6.....	20	0·9328	15·80	16·87	20·27	52·87	169·38	180·86	217·30	566·79	575·0	613·9	737·7	1924·0	3·346	1·283	2·608
$CHCl_3$	20	1·0936	16·81	17·76	21·35	55·23	153·71	162·40	195·23	505·03	521·7	551·2	662·5	1714·0	3·285	1·270	2·586
l-*Menthyl* 4-*Chloro*-2-*nitrobenzoate*.																	
CS_2	20	0·8248	11·93	12·60	14·99	36·90	144·64	152·76	181·74	447·38	491·1	518·6	617·0	1518·9	3·093	1·256	2·462
l-*Menthyl* 4-*Chloro*-3-*nitrobenzoate*.																	
C_5H_5N	10	0·9203	3·34	3·46	3·93	7·15	72·57	75·19	85·41	155·39	246·3	255·3	289·9	527·4	2·141	1·177	1·820
l-*Menthyl* 2 : 6-*Dinitrobenzoate*.																	
C_6H_6.....	10	0·9451	8·78	9·39	11·33	30·75	184·05	196·83	237·49	644·60	644·3	689·2	831·6	2256·0	3·501	1·290	2·713
l-*Menthyl* 2 : 4-*Dinitrobenzoate*.																	
C_5H_5N	10	0·9453	5·48	5·78	6·85	16·43	116·0	122·6	145·0	347·62	405·9	428·8	507·4	1116·7	2·997	1·250	2·398
CS_2	10	0·9660	6·44	6·82	8·11	19·47	133·3	141·2	167·9	403·11	466·7	494·2	587·6	1410·9	3·024	1·262	2·401
$CHCl_3$	10	0·9887	6·72	7·12	8·45	19·96	135·9	144·0	170·9	403·76	475·7	504·1	598·2	1413·2	2·970	1·257	2·362
C_6H_6.....	10	0·9599	6·63	7·01	8·33	20·43	138·1	146·1	173·6	425·68	483·5	511·1	607·4	1489·8	3·081	1·256	2·452
l-*Menthyl* 3 : 5-*Dinitrobenzoate*.																	
$CHCl_3$	20	0·9279	7·46	7·73	8·91	16·13	80·39	83·32	96·03	173·83	281·4	291·6	336·1	608·4	2·162	1·195	1·810
***m*-*Tolyl*-l-*menthylcarbamide*.**																	
C_5H_5N	22	0·4453	4·04	4·26	4·86	8·58	80·67	85·06	97·03	171·32	233·1	245·8	280·4	495·1	2·123	1·202	1·766

TABLE II. (*continued*).

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	α_{ye}.	α_{gr}.	α_{vi}.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	$Hg\frac{violet}{green}$.
2-*Naphthyl*-l-*menthylcarbamide*.																	
$CHCl_3$	22	0·2263	1·61°	1·69°	1·91°	3·39	64·68°	67·89°	76·72°	136·18°	209·5°	220·0°	248·5°	441·2°	2·106	1·187	1·775
1-*Naphthyl* l-*Menthylcarbamate*.																	
$C_2H_5{\cdot}OH$.	10	0·6207	1·51	1·61	1·82	3·11	48·66	51·86	59·64	100·20	157·1	167·5	189·4	323·6	2·060	1·250	1·710
l-*Menthyl* 2-*Methoxynaphthoate*.																	
CS_2	10	0·9894	2·32	2·44	2·79	4·42	46·89	49·32	56·39	89·33	159·4	167·7	191·2	303·8	1·905	1·204	1·584
C_6H_6.....	22	1·0045	5·65	5·90	6·71	11·02	51·16	53·43	60·75	99·79	174·0	181·7	206·5	339·3	1·951	1·188	1·643
Pyridine Salt of l-*Menthyl Hydrogen Phthalate*.																	
C_5H_5N	20	1·3140	9·32	9·80	11·34	20·99	70·92	74·57	86·30	159·74	264·5	278·2	321·9	595·8	2·252	1·217	1·851
Sodium Salt of l-*Menthyl Hydrogen Phthalate*.																	
H_2O	22	1·0590	7·06	7·37	8·43	14·42	60·74	63 42	72·52	123·79	192·0	200·4	229·2	392·1	2·043	1·194	1·711
Mixed Hydrogen Phthalates of l-*Menthol and* d-*Neomenthol* (T., 1912, **101**, 126).																	
CS_2	22	1·0154	+3·18	+3·34	+3·82	+7·07	+28·48	+29·91	+34·22	+63·33	—	—	—	—	2·224	1·201	1·850
$C_2H_5{\cdot}OH$...	22	1·0307	+3·37	+3·51	+4·04	+7·34	+29·72	+30·95	+35·63	+64·73	—	—	—	—	2·178	1·199	1·817
$CHCl_3$	20	0·9429	+3·76	+4·02	+4·62	+8·19	+39·87	+42·63	+48·99	+86·85	—	—	—	—	2·183	1·228	1·773
C_6H_6.....	20	0·9543	+4·52	+4·70	+5·40	+9·96	+47·37	+49·26	+56·59	+104·37	—	—	—	—	2·204	1·195	1·845

TABLE II. (*continued*).

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_D$.	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_D$.	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$	Dispersion ratios. $\frac{Hg_{violet}}{Na_{yellow}}$.	$\frac{Hg_{green}}{Na_{yellow}}$.	$Hg\frac{violet}{green}$.
l-*Menthone*.																	
C_6H_6.....	20	1·0037	1·68°	1·72°	1·99°	3·53°	16·73°	17·13°	19·83°	35·17°	25·6°	26·2°	30·3°	53·8°	2·101	1·185	1·774
C_2H_5·OH...	20	1·0990	2·55	2·64	3·04	5·20	23·19	24·02	27·66	47·31	35·5	36·8	42·3	72·4	2·039	1·192	1·710
CS_2	20	1·0944	2·62	2·72	3·18	6·42	23·95	24·86	29·07	58·68	36·6	38·1	44·5	89·8	2·450	1·213	2·018
d-iso*Borneol*.																	
C_2H_5·OH...	22	1·0328	+3·85	+4·02	+4·50	+7·42	+33·89	+35·38	+39·61	+65·31	+52·2	+54·5	+60·9	+100·6	1·927	1·169	1·649
$CHCl_3$	20	0·9987	+2·02	+2·09	+2·33	+3·70	+20·33	+20·92	+23·33	+37·05	+31·2	+32·2	+35·9	+57·1	1·831	1·153	1·588
l-*Borneol*.																	
C_2H_5·OH...	22	1·1020	4·46	4·74	5·40	9·22	36·79	39·10	44·54	76·05	56·6	60·2	68·6	117·1	2·069	1·211	1·707
l-iso*Bornyl Hydrogen Phthalate*.																	
$CHCl_3$	20	1·0653	8·25	8·60	9·88	17·40	77·47	80·74	92·76	163·34	234·0	243·9	280·2	493·3	2·109	1·199	1·759
C_2H_5·OH...	20	1·0391	8·48	8·86	10·18	18·05	81·62	85·27	97·97	173·71	246·5	257·5	295·9	524·7	2·128	1·200	1·773
d-*Bornyl Hydrogen Phthalate*.																	
C_6H_6.....	20	0·9553	+4·08	+4·30	+4·96	+8·76	+42·72	+45·02	+51·93	+91·70	+129·0	+135·9	+156·8	+277·0	2·147	1·215	1·766
CS_2	20	0·3300	+1·52	+1·56	+1·71	+3·20	+46·06	+47·28	+51·82	+96·96	+139·1	+142·8	+156·5	+292·8	2·105	1·216	1·871
C_2H_5·OH...	20	1·0364	+5·88	+6·19	+7·09	+12·81	+56·72	+59·71	+68·39	+123·60	+171·3	+180·3	+206·5	+373·2	2·178	1·206	1·807

Further observations of density, D'_4, and rotatory power ($\alpha_{100\ mm.}$) of substances examined in the homogeneous state.

l-*Menthol.*

Temp.	35°	55°	74°	79°	104°	126°	159°	197°
α_D	−43·90	43·60	42·96	42·62	41·22	39·68	37·72	35·60
Temp.	37°	42°	54°	71°	100°	126°	159°	196°
α_{ye}.....	−46·12	46·04	45·68	44·94	43·06	41·50	39·44	37·90
Temp.	36°	43°	53°	71°	100°	126°	159°	196°
α_{gr}	−52·08	52·02	51·80	50·90	48·66	46·90	44·52	42·20
Temp.	35°	44°	52°	72°	100°	126°	159°	
α_{vi}.....	−86·54	86·10	85·84	84·38	81·14	78·10	74·16	

l-*Menthyl Acetate.*

Temp.	17°		61°	96°	132°		
Density	0·9287		0·8914	0·8617	0·8294		
Temp.	16·5°	25°	60°	80°	108°	147°	167°
α_D	−73·82	73·20	70·38	68·86	66·68	63·76	62·14
Temp.	16·5°	—	65°	83°	108°	147°	167°
α_{ye}.....	−77·16	—	73·14	71·62	69·70	66·54	64·64
Temp.	16·5°	—	62°	83°	108°	147°	167°
α_{gr}.....	−87·54	—	83·16	81·22	78·92	75·46	73·54
Temp.	16·5°	—	67°	85°	110°	147°	167°
α_{vi}.....	−145·06	—	137·36	134·82	131·50	125·50	121·30

Di-l-*menthyl Oxalate.*

Temp.	19°		54°		91°		138°	
Density	0·9849		0·9566		0·9265		0·8905	
Temp.	20°	53°	56°	90°	125·5°	140°	164°	194°
α_D	−91·86	89·20	89·00	86·12	82·74	81·06	79·18	76·00
Temp.	20°	59°	80°	125°	140°	164°	194°	
α_{ye}.....	−95·92	92·60	90·76	86·34	84·60	82·46	79·16	
Temp.	20°	60°	80°	125°	140°	164°	194°	
α_{gr}	−108·52	104·64	102·50	97·82	95·94	93·46	89·64	
Temp.	20°	61°	80°	125°	140°	164°	194°	
α_{vi}.....	−179·00	172·62	169·02	161·58	159·00	154·70	149·16	

l-*Menthyl Phenylacetate.*

Temp.	21°	63°	99°	149°	173°
α_D	− 68·22	64·48	60·82	56·42	54·52
Temp.	21°	60°	99°	149°	176°
α_{ye}.....	− 71·32	67·60	63·52	58·96	56·82
Temp.	21°	60°	99°	149°	176°
α_{gr}	− 18·18	76·86	72·24	76·20	64·44
α_{vi}.....	−137·60	129·90	122·26	113·10	107·90

l-*Menthyl* p-*Methoxybenzoate.*

Temp.	19°	60·5°	123°	150°	175°
α_D	— 89·46	84·36	77·20	73·94	71·34
Temp.	19°	56°	122°	151°	176°
α_{ye}.....	— 93·52	88·66	80·70	77·20	74·56
Temp.	19°	57°	123°	151°	176°
α_{gr}.....	—106·48	100·70	91·44	87·60	84·38
Temp.	19°	55°	122°	151°	176°
α_{vi}.....	—181·14	170·70	153·60	147·40	141·60

l-*Menthyl* o-*Iodobenzoate.*

At 19°..... α_D —84·36. α_{ye} 88·40. α_{gr} 101·16. α_{vi} 179·82
At 70·5° ... α_D —81·18. α_{ye} 85·00. α_{gr} 97·32. α_{vi} 173·38

l-*Menthyl* m-*Iodobenzoate.*

At 19°..... α_D —42·12. α_{ye} 43·96. α_{gr} 50·00 α_{vi} 83·80

l-*Menthyl* p-*Iodobenzoate.*

At 19°..... α_D —41·74. α_{ye} 43·62. α_{gr} 49·40. α_{vi} 83·10

l-*Menthyl* o-*Nitrobenzoate,* b. p. 185°/2 mm.

Temp.	22·5°	25°	38°	56°	104°	126°	153°	184°
α_D	—142·78	142·44	138·80	134·52	123·96	120·22	115·56	110·16
Temp.	22·5°	28°	58°	84°	97°	121°	133°	153°	186°
α_{ye}	—151·40	149·90	142·00	135·30	131·92	127·10	125·18	122·00	116·26
Temp.	22·5°	28°	34°	60°	84°	100°	121°	153°	186°
α_{gr}	—178·90	177·64	175·10	166·80	159·80	154·70	150·08	143·66	136·46
Temp.	22·5°	28°	33°	56°	80°				
α_{vi}	—423·0	420·2	417·0	395·0	375·6				

l-*Menthyl* m-*Nitrobenzoate,* b. p. 186°/2 mm.

Temp.	19°	56°	65°	87°	102°	149°	182°
α_D	— 92·22	88·66	88·00	85·56	84·00	79·04	76·98
Temp.	19°	62°	65°	80°	109°	149°	182°
α_{ye}	— 96·44	92·20	91·82	90·24	86·84	82·76	80·72
Temp.	19°	62°	66°	80°	109°	149°	182°
α_{gr}	—109·94	105·00	104·41	102·66	99·08	94·36	91·50
α_{vi}.....	—193·94°.						

l-*Menthyl* p-*Nitrobenzoate,* b. p. 192°/3 mm.

Temp.	22°	25°	39°	63°	75°	118·5°	159°	187°
α_D	—79·32	79·20	78·10	76·10	75·18	71·86	68·70	66·78
Temp.	22°	30°	39°	73°	85°	118°	162°	187°
α_{ye}.....	—82·70	82·22	81·50	78·74	77·76	74·92	71·68	69·70
Temp.	22°	32°	39°	74°	86°	118°	163°	187°
α_{gr}.....	—93·20	92·44	91·90	88·72	87·44	84·56	80·86	78·66

l-*Menthyl* p-*Allyloxybenzoate.*

At 20°..... α_D —81·92 α_{ye} 85·80. α_{gr} 96·68. α_v 165·20

l-*Menthylamine.*

Temp.	17°	54°	94°	133°
Density ...	0·8567	0·8307	0·7976	0·7657
Temp.	19°	47°	98°	137°
a_D	−34·20	34·28	34·02	33·58
a_{ye}.....	−35·62	35·70	35·50	34·90
a_{gr}.....	−40·26	40·36	40·00	39·44
a_{vi}.....	−65·38	65·58	65·52	64·48

l-*Menthone.**

Temp.			18°	54°	94·5°		129°	
Density			0·8968	0·8692	0·8362		0·8073	
Temp.	21°	34°	60°	76°	100°	129°	145°	167°
a_D	−24·00	24·10	24·40	24·62	25·18	25·62	25·22	24·76
Temp.	21°	34°	56°	77°	100°	128°	145°	167°
a_{ye}.....	−25·00	25·14	25·52	25·84	26·38	26·86	26·46	25·86
Temp.	21°	34°	56°	77°	100°	128°	145°	167°
a_{gr}.....	−28·80	28·98	29·42	29·88	30·60	31·14	30·64	30·20
Temp.	21°	34°	56°	77°	100°	128°	145°	167°
a_{vi}.....	−51·34	52·06	53·64	54·64	57·02	58·68	57·46	55·94

*Menthone A.**

At 19°..... a_D +3·36. a_{ye} +3·82. a_{gr} +5·04. a_{vi} +18·26

*Menthone B.**

At 20°..... a_D +10·38. a_{ye} +11·06. a_{gr} +13·66. a_{vi} +36·00

*Menthone C.**

At 20°..... a_D −16·82. a_{ye} −17·50. a_{gr} −19·86. a_{vi} −32·54

* See footnote to Fig. 4, page 43.

l-*Bornyl Acetate.*

Temp.		17·5°	52°	98°	133·5°	
Density		0·9879	0·9597	0·9169	0·8840	
Temp.	16·5°	40°	73°	94°	135°	167°
a_D	−42·26	39·42	35·72	34·00	30·30	28·02
Temp.	16·5°	41°	72°	92°	133°	167°
a_{ye}	−43·98	41·02	37·40	35·60	31·90	29·20
Temp.	16·5°	42·°	72°	92°	133°	167°
a_{gr}	−50·00	46·36	42·44	40·36	36·24	33·00
Temp.	16·5°	42°	71°	92°	133°	167°
a_{vi}	−84·10	78·00	71·14	67·70	60·78	55·42

The authors desire to express their thanks to Mr. John Ranson for able assistance, and desire to state that many of the compounds used in this investigation were prepared from material the cost of which was defrayed by grants received from the Government Grant Committee of the Royal Society.

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VIII.—*The Atomic Weight of Tin.*

By Henry Vincent Aird Briscoe.

Numerous determinations of the atomic weight of tin have been made, and, as a necessary preliminary to any account of the present investigation, the methods and results of these researches will be briefly indicated.

The investigations of Gay Lussac (*Ann. Chim. Phys.*, 1811, **80**, 160), Berzelius (*Ann. Phys. Chem.*, 1826, [ii], **8**, 177), Mulder and Vlaanderen (*J. pr. Chem.*, 1849, **49**, 35), and Dumas (*Ann. Chim. Phys.*, 1859, [iii], **55**, 154) were made by the oxidation of tin with nitric acid. Dumas also made two determinations of the ratio $SnCl_4 : 4Ag$ by titration (the method of the present investigation), but regarded them merely as of confirmatory value. Vlaanderen, later (*Jahresb.*, 1858, 183), found certain errors in the method of oxidising tin with nitric acid, and, therefore, determined the ratio $Sn : SnO_2$ by reducing stannic oxide in hydrogen. Van der Plaats (*Compt. rend.*, 1885, **100**, 52) employed both these methods for the measurement of the oxide ratio.

Two comparatively recent determinations of the ratio $Sn : SnO_2$ by oxidation of tin have been made incidentally in the course of other work by Schmidt (*Ber.*, 1894, **27**, 2743) and by Meyer and Kerstein (*Ber.*, 1913, **46**, 2882).

The research of Bongartz and Classen (*Ber.*, 1888, **21**, 2900) is by far the most considerable attempt that has hitherto been made to fix the atomic weight of tin. Their work involved the measurement of five ratios, namely, $Sn : SnO_2$; $SnBr_4 : Sn$; $K_2SnCl_6 : Sn$; $(NH_4)_2SnCl_6 : Sn$; and $Sn : 2BaSO_4$.

Their starting material was Banca tin, from which the tetrachloride was prepared by the action of dry chlorine. The product was fractionated repeatedly, and the fraction boiling constantly at 120°* collected for use.

In the determination of the oxide and barium sulphate ratios the metallic tin required for conversion into oxide or sulphide was obtained as follows: The purified stannic chloride was dissolved in water, and treated, with constant stirring, with a concentrated solution of crystallised sodium sulphide until the precipitate redissolved, and a solution of sodium hydroxide equal in amount to about half the sodium sulphide used was then added. After some days the solution had become quite clear; and it was then electro-

* The boiling point here given is 6° higher than that determined by Thorpe (T., 1880, **37**, 331).

lysed in a weighed platinum dish or crucible. The deposit of metallic tin was washed with water and alcohol, dried at 100°, cooled over phosphoric oxide, and weighed.

In the determination of the ratio Sn : $2BaSO_4$ a very complicated analytical procedure was used, of which only an outline is given. The results are stated merely as percentages of sulphur, but, assuming that these are based on the atomic weights of Meyer and Seubert, it is possible to calculate the weights of barium sulphate actually obtained.*

The potassium and ammonium stannichlorides were also prepared from the same stannic chloride, and the percentage of tin they contained was determined by electrolysis of their solutions in aqueous ammonium oxalate at 30—40° and at the ordinary temperature respectively.

The ratio of tin to stannic bromide was determined by electrolysis of a solution of stannic bromide containing ammonium oxalate.

TABLE I.

No.	Date.	Investigator.	Ratio measured.	No. of Detns.	Result: Sn = (O = 16)	Average error.
1	1811	Gay-Lussac	Sn : SnO_2 (oxidation)	—	117·7	—
2	1826	Berzelius				
3	1849	Mulder & Vlaanderen	Sn : SnO_2 ,,	3	116·3	0·32
4	1859	Dumas	Sn : SnO_2 ,,	2	118·06	0·15
5	1885	van der Plaats ...	Sn : SnO_2 ,,	3	118·08	0·04
6	1894	Schmidt.....	Sn : SnO_2 ,,	1	118·49	—
7	1913	Meyer & Kerstein	Sn : SnO_2 ,,	2	117·54	0·12
8	1858	Vlaanderen	Sn : SnO_2 (reduction)	2	118·16	0·08
9	1885	van der Plaats.....	Sn : SnO_2 ,,	4	118·07	0·05
10	1859	Dumas	$SnCl_4$: 4Ag	2	117·97	0·04
11	1888	Bongartz & Classen	Sn : SnO_2 (oxidation)	11	119·06	0·144
12	1888	Bongartz & Classen	Sn : $2BaSO_4$	8	119·08	0·075
13	1888	Bongartz & Classen	Sn : $(NH_4)_2SnCl_6$	16	119·09	0·076
14	1888	Bongartz & Classen	Sn : K_2SnCl_6	10	119·07	0·035
15	1888	Bongartz & Classen	Sn : $SnBr_4$	10	118·98	0·040

The results of the determinations quoted above are collected in table I. Inspection will show that they may be divided into two classes; on the one hand, the determinations of Bongartz and Classen, giving a mean result of Sn = 119·06, and on the other the rest of the determinations, which all give values for the atomic weight less than 118·5. Of the latter results the analyses of Gay Lussac, Berzelius, and Mulder and Vlaanderen appear to be low as compared with those of Dumas, Vlaanderen, and van der Plaats,

* The antecedent data used throughout this paper are: Ag = 107·880, Cl = 35·457 and Cl = 35·460, Br = 79·920, N = 14·010, S = 32·067, Ba = 137·363, H = 1·00779. Where the higher value for chlorine, Cl = 35·460, is used, a statement to that effect is made; in all other cases the use of the lower value is to be understood.

which approximate to 118. If anything at all can be inferred from the figures it is that the atomic weight of tin is near 118·0.

The five series of fairly concordant measurements by Bongartz and Classen, however, indicate that the atomic weight of tin is greater than 119·0.

It is extremely difficult to decide between these two values, but the International Committee on Atomic Weights and Clarke in his "Recalculation of the Atomic Weights" reject all determinations other than those of Bongartz and Classen, on whose value they base the accepted figure Sn = 119·0.

A further discussion of these data will be made in connexion with the statement of the results of this investigation, but enough has been said to show the urgent need for new determinations of the atomic weight of tin.

Outline of the Present Investigation.

Tin forms few definite compounds that can be purified by distillation or by crystallisation and fusion, and the chief of these—the chloride and bromide—present peculiar difficulties in manipulation on account of their sensitiveness to moisture. It is probably for this reason that these substances have been so little used in researches on the atomic weight of tin, and that preference has been given to the determination of the ratio SnO_2 : Sn. The variation in the results obtained is a measure of the uncertainty of the latter method.

Of all the compounds of tin, stannic chloride would appear to be the most suitable for use in the determination of the atomic weight of the metal, provided that proper steps are taken to protect it from atmospheric moisture. It is very stable, it can be prepared easily, and it can be completely purified without great difficulty provided water be excluded rigidly. Moreover, the proportion of tin to chlorine in this compound is such that a given error in the determination of the percentage of the latter element produces a much smaller error in the atomic weight of tin than would an equal error in the determination of the ratio Sn : SnO_2 (see table IV).

The present re-determination of the atomic weight of tin has therefore been effected by measurement of the ratio $SnCl_4$: 4Ag.

Stannic chloride was prepared by direct union of its elements, and purified by fractional distillation. A portion of the final fraction of this purified material was further fractionated twice, and collected in weighed bulbs in a sealed and exhausted apparatus. The solutions for analysis were prepared by breaking the bulbs in dilute nitric acid containing either oxalic acid or tartaric acid, and were then treated with a slight deficit of silver nitrate prepared

by dissolving a weighed amount of silver in nitric acid. The slight deficit of silver was made up by addition of a measured volume of a dilute standard silver solution, and the titration was completed by the further addition of dilute standard silver or sodium chloride solution. The progress of the titration and the attainment of the end-point were ascertained by nephelometric measurements, which were carried out by the same method and in the same apparatus as was described in a former communication (Briscoe and Little, T., 1914, **105**, 1321). In this way fifteen distinct fractions of stannic chloride were analysed.

The chief difficulties arose from (1) the sensitiveness to moisture of the stannic chloride, and (2) the rapid hydrolysis of that compound in dilute aqueous solution. Of these the first was completely and satisfactorily overcome by the special methods of distillation and weighing employed in previous work on the atomic weight of vanadium (Briscoe and Little, *loc. cit.*), and the second was met by the addition of oxalic acid, or, in one case, tartaric acid (Rochelle salt) to the solutions.

The conditions of the titrations, the amounts of the various reagents used, and the details of manipulation were varied from one experiment to another, with the object of eliminating possible constant errors due to such sources, and all the usual precautions were carefully observed.

Preparation and Purification of Reagents.

The purification of all reagents received very special attention, and those used in the analyses were frequently tested throughout the course of the work. In the following paragraphs the methods by which each reagent was purified or obtained are described in detail.

Water.—In the course of the determinations it has been found that water of an extremely high degree of purity as regards freedom from chlorine can be obtained in one distillation from tap-water if a still of the domed-condenser type is used. During the vacation the laboratory supply of distilled water, which is obtained from such a still, was free from chlorine, and was, accordingly, used in the purification of several of the reagents. During the time students were in the laboratory in which the still is situated the water was found to be slightly contaminated with chlorine, derived, presumably, from the air of the laboratory, and at such times all the water used was further purified. In all cases except one, specially purified water was used in the preparation of the solutions for analysis.

For the further purification of the water it was distilled from

a large copper vessel with the addition of a trace of sodium carbonate, and the steam was led through a wide copper tube in order to diminish spraying, and condensed in a long tube of pure tin. The water was kept during the brief period before use in well-stoppered bottles of Jena glass.

Hydrochloric Acid.—This reagent was required free from arsenic for the preparation of pure hydrogen. It was therefore treated with a copper–tin couple, and distilled from copper gauze according to Thorne and Jeffers' method (*Analyst*, 1906, **31**, 101).

Zinc.—Granulated electrolytic zinc, supplied through the kindness of Messrs. Brunner, Mond and Co., Ltd., proved to be free from arsenic, and was therefore used without further purification.

Hydrogen.—This gas was prepared by the action of dilute hydrochloric acid on zinc in a Kipp's apparatus. A small quantity of platinic chloride was added to the acid to facilitate the action. The hydrogen generated was bubbled through a long column of potassium hydroxide solution, and then passed over solid potassium hydroxide and finally over phosphoric oxide. The gas issuing from the purifier was tested by passing it through a Jena-glass tube drawn out to a capillary, and heated to redness in the wider portion immediately adjacent thereto. The longest run—of five hours at the rate of 3 litres per hour—gave no visible deposit in the capillary, and the gas must, therefore, have been free from arsenic.

Magnesia.—Pure magnesia was prepared by repeated precipitation of magnesium carbonate from magnesium nitrate solution by means of pure sodium carbonate; the precipitate was washed thoroughly, dried, and ignited in an electrically-heated muffle furnace (compare Briscoe and Little, *loc. cit.*).

In making new magnesia boats for these determinations some little difficulty was experienced, as some of the boats cracked and were very friable after ignition. Numerous trials ultimately showed that good results could be consistently obtained if the boats were moulded with the walls not less than 3 mm. thick. The strongest boats were those made with the powdered fragments of old boats mixed with about one-sixth of their bulk of fresh magnesia. The last traces of sulphur were removed from the boats by igniting them for several hours in a stream of hydrogen containing a little water vapour.

During all fusions of silver the hydrogen issuing from the furnace was examined, and was found in every case to be quite odourless. This fact affords good evidence of the purity of both the hydrogen and the magnesia as the probable dangerous impurities, namely, sulphur and arsenic, would be indicated by the presence in

the gas of arsine and hydrogen sulphide, both of which can be detected by smell when present in extremely minute quantities.

Nitric Acid.—The purest nitric acid of commerce was redistilled twice from a glass flask with ground connexions, and in each distillation the first half of the distillate and a small end-fraction were rejected.

Oxalic Acid.—Two samples of oxalic acid were prepared by recrystallisation of the purest commercial substance according to the following plan. A boiling saturated solution of the acid in pure water was filtered through a hot funnel, re-heated in order to dissolve the crystals formed, and then cooled as rapidly as possible with violent agitation. The mother liquor was carefully decanted from the crystals, and the latter were then divided into two approximately equal parts and wrapped in two pieces of clean linen. These bundles of crystals were then placed on opposite sides of the copper basket of a centrifuge, and whirled at 2000 revolutions per minute, which, with a basket 28 cm. in diameter, corresponds with a peripheral speed of 1770 metres per minute. The crystals were then again dissolved, recrystallised, and drained, and the process was repeated three times in the case of one sample (oxalic acid I) and six times in another case (oxalic acid II). All the operations were carried out in porcelain vessels.

The linen cloths used were cleansed originally by boiling with dilute ammonia for an hour and then washing with water in a Soxhlet extraction apparatus for forty-eight hours. Between recrystallisations the cloths were similarly washed for a period of at least two hours (twenty-four to twenty-eight washings).

It was found impossible to detect by means of the nephelometer any trace of chloride in either sample of the oxalic acid.*

Rochelle Salt.—Commercial recrystallised Rochelle salt was recrystallised four times by a method precisely similar to that described above for oxalic acid. Nephelometric tests showed the product to be free from chloride.

Chlorine.—The chlorine used for the preparation of stannic chloride was obtained from the middle fraction remaining after 15·75 kilos. had been evaporated from 43·2 kilos. originally contained in a steel cylinder of the liquefied gas.

Ammonia Solution.—This was prepared by dissolving in pure water ammonia expelled from the purest commercial ammonia

* Centrifugal extraction of the mother-liquor under the conditions described was remarkably effective. The crystals appeared loose and dry when taken from the centrifuge and could have contained only a very small amount of water as the final crop some 1500 grams, dried completely in six hours' exposure to air in a covered dish.

(D 0·880) by heating it to about 50°. The operation was performed in vessels of Jena glass.

Sulphur Dioxide.—Gaseous sulphur dioxide was obtained from the middle fraction of a syphon of the liquid. Its further purification was unnecessary as the presence of a trace of chlorine in this material would not adversely affect the purity of the silver prepared by its aid.

Formic Acid.—Kahlbaum's purest formic acid was redistilled in platinum and collected in a platinum bottle.

Ammonium formate was prepared in solution by neutralising pure formic acid with ammonia solution prepared by the solution in pure water of ammonia gas expelled by heat from ammonia solution prepared as above described, the whole operation being conducted in platinum vessels.

Silver.—Five samples of pure silver were prepared, four by reduction of an ammoniacal solution of silver with ammoniacal cuprous sulphite solution, according to Stas' method, and one by reduction of pure silver nitrate with ammonium formate as described by Richards and Wells (*J. Amer. Chem. Soc.*, 1905, **27**, 459). The main details of these preparations are as follows:

Sample I.—A solution of 200 grams of recrystallised silver nitrate was mixed with a solution of 15 grams of electrolytic copper in nitric acid, and treated with ammonia solution until the precipitate first formed had redissolved. This solution was diluted to about 10 litres.

Meanwhile a solution of ammonium sulphite had been prepared by neutralising with sulphur dioxide a solution of approximately 100 grams of ammonia in 2 litres of water. This solution, while still warm (approx. 40°), was added to the prepared silver solution, and the whole was well shaken and kept in a stoppered bottle. After twenty-four hours all the silver had been deposited as a crystalline precipitate, and the solution was nearly colourless.

The supernatant liquid was poured off, and the silver was washed six times with water, allowed to remain for twelve hours with dilute ammonia solution, then washed again six times with water, and finally transferred to a large platinum dish, in which it was washed three times with water and, finally, drained as completely as possible and dried in the dish by heating at 250° in an electrically-heated air-bath.

Sample II.—Residues of silver chloride obtained in the determination of a previous atomic weight were dissolved in dilute ammonia, and the solution filtered and treated with ammonium sulphite prepared as for sample I, the temperature being raised to

70°. The silver produced was thoroughly washed and united with a quantity of silver, which had been prepared previously, and the whole dissolved in nitric acid. The filtered solution was then reduced as before, except that the reduction only became complete after long heating to 70°.

It may here be remarked that in this process of reduction the rate of deposition of silver, the density of the product, etc., vary considerably with the concentration of free ammonia and copper in the solution. There can be no doubt that the product is in every case silver of the same high order of purity, but an investigation of the reaction would probably be of interest.

Sample III of silver was prepared by the same method as samples I and II from silver nitrate which had been thrice recrystallised from water with centrifugal drainage. The excess concentration of ammonia was kept low, and a finely crystalline precipitate of silver quickly formed. The silver was washed and dried as before.

Sample IV.—A portion of sample I was dissolved in nitric acid and reprecipitated by the method described above. In this case the excess concentration of ammonia was considerable, and the precipitation of silver took about three times as long as in the preparation of sample III.

Sample V.—Silver nitrate which had been twice recrystallised from water was reduced with ammonium formate. The product was washed as in the case of the other samples, and dried at 300°.

In every case the silver was prepared for weighing by fusion in a magnesia boat in a stream of hydrogen. The fused metal was cooled in hydrogen, etched for five to ten minutes in diluted nitric acid, washed thoroughly with water, dried at 300° for twelve hours, and cooled in a desiccator over potassium hydroxide. The weight of silver was adjusted by adding pieces of silver wire drawn from buttons of pure silver with the precautions previously described (Briscoe and Little, *loc. cit.*).

Stannic Chloride.—According to the analyses of Mulder (*J. pr. Chem.*, 1849, **49**, 35) and van der Plaats (*Compt. rend.*, 1885, **100**, 52) the common impurities of Banca tin are iron, copper, lead, and silica. In the preparation of stannic chloride by the action of chlorine on tin it is found that the silica is left unattacked; whilst it seems probable that in the presence of an excess of tin any copper chloride formed would be again decomposed as copper is notably electronegative to tin.

Supposing iron, copper, and lead chlorides to be formed they should be easily separated from the main product by reason of the differences between their boiling points and that of stannic

chloride ($SnCl_4$, 114°; $FeCl_3$, 448°; $FeCl_2$, about 1100°; CuCl, about 1000°; $CuCl_2$, decomposes; $PbCl_2$, 860°). Further, if stannous chloride were formed it also should be completely separated by fractional distillation, as it boils at 606°. The following method of preparing and purifying stannic chloride was therefore employed.

About 1 kilo. of good commercial granulated tin was treated, in quantities of about 250 grams at a time, with chlorine gas. The reaction was carried out in a round Jena-glass flask provided with a long, air-cooled condenser, and the current of chlorine was so regulated as to keep the stannic chloride gently boiling. No external source of heat is required.

The product (about 1800 grams) was kept in contact with metallic tin for forty-eight hours, and then distilled three times in an apparatus constructed entirely of glass, rejecting in each distillation the first and last quarters of the distillate. The final main fraction of about 400 grams boiled constantly at 113·9—114·1°.

After being kept for some time all the fractions of stannic chloride, but especially the earlier fractions, deposited small quantities of a colourless, crystalline substance, which was probably the hydrate $SnCl_4,3H_2O$.

During the earlier stages of the fractionation, which involved some contact of the stannic chloride with air, it was found to be impossible to eliminate this impurity completely. Attempts to remove this water by distillation with metallic sodium failed, as it was found that even in an atmosphere of carbon dioxide the material exploded as soon as the boiling point was reached.

The Determination of Weight.

All the weighings involved in the determinations now under consideration were made on a short-beam Bunge balance, which was set aside especially for this work, and was placed in a special room entirely contained within another room, their walls and roofs being separated by an air space several feet wide. This room is situated in the interior of a section of the building which has special foundations designed to insulate it from all vibration. The temperature of this balance-room did not vary half a degree during nine months, and to this fact and to the absence of vibration must be attributed the remarkably constant behaviour of the balance.

The sensitiveness of the balance was so adjusted that the zero shifted about nine scale divisions for a difference in weight of 1 milligram, and the excursions of the pointer were read with the

aid of a lens. In weighing, the rider was adjusted to within two- or three-tenths of a milligram of the apparent weight, and the remaining tenths and hundredths of a milligram to be added or subtracted in order to get the true apparent weight were determined by the method of oscillations.

A set of gilt brass weights with platinum fractions by Becker, and a gold five-milligram rider were used; they were calibrated carefully both before and during the course of the work in order to determine their relative weights in air. The relative weights in a vacuum were not calculated, for the reasons given in a former paper (Briscoe and Little, *loc. cit.*), and the vacuum correction applied to the apparent weight of the silver (D 10·49) was +0·000117 gram per gram.

All weighings were made by reversal, and two separate approximate weighings were also made, one on an ordinary balance and one on the special balance. A double check was thus provided against any error in the recording of the weight.

In many cases the precise weighings were made in duplicate, but in no instance did the separate values for the vacuum weight differ by more than 0·00002 gram. All weighings of bulbs were made against a tare consisting of a similar bulb and stem in which the capillary between the bulb and stem was sealed. The air in the balance case was dried by solid potassium hydroxide, and the bulbs were kept in this dried atmosphere for several hours previous to the determination of their weight. To ensure the dissipation of any electrical charge induced on the surface of the glass when it was cleaned, a piece of pitch-blende was kept in the balance case. In all cases the weight of stannic chloride was corrected for the weight of air displaced from the bulb, the magnitude of this correction being determined by the method described in a former communication (Briscoe and Little, *loc. cit.*). As the pans of the balance were of glass, the buttons of silver were weighed directly on them.

The weights of stannic chloride are stated to the nearest twentieth of a milligram; those of silver to the nearest tenth of a milligram. It will readily be understood that the actual weighings of silver are more precise than is stated, but that the accuracy of the determination of the total weight of silver required depends on the precision with which the end-point of the titration can be found. With the concentrations used it was possible, if the solutions were kept at about 10°, to ascertain the end-point within one-tenth of a milligram of silver, and the weights of silver are, therefore, stated to that degree of accuracy.

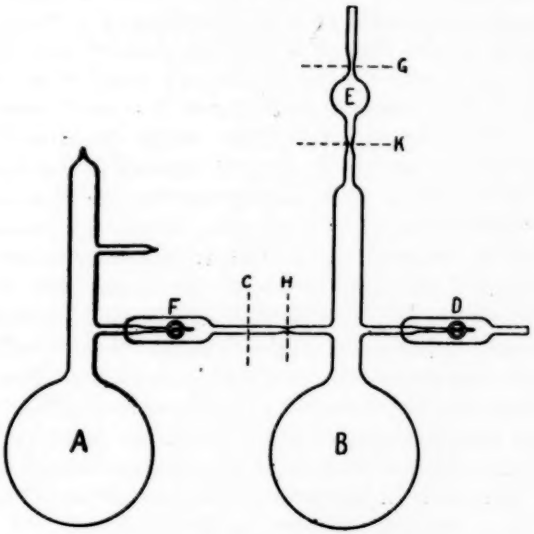
It is evident that the errors in the weights of stannic chloride

and silver are less than 1 part in 150,000, and, therefore, insignificant in comparison with the other errors of the determinations.

Purification of Stannic Chloride and its Collection in Bulbs.

In the final purification of stannic chloride about 150 c.c. (330 grams) of the end-fraction previously obtained (p. 71) was placed in a flask of 250 c.c. capacity, together with about 2 grams of metallic tin. This flask had a long neck, which was closed by fusion at the upper end after the introduction of the chloride, and had two side-tubes, one of which carried a special joint (Briscoe and Little, *loc. cit.*), whilst the other was open, but constricted

FIG. 1.



at one point. By means of a Gaede pump, the flask was exhausted through this second tube, which was then sealed off at the constriction. The flask thus sealed was entirely immersed in a steam-bath and heated to 100° for four hours.

After the heating a white sublimate of the crystalline hydrate previously referred to was observed in the upper part of the flask, and, although it was present in a very small amount, it seemed desirable to remove it. This sublimate appeared to be firmly attached to the walls of the flask, and the greater part of it was separated from the liquid by decanting the latter into a second flask. The apparatus used is shown in Fig. 1.

By heating the first flask *A* the volatile hydrate was driven into the upper part of the neck, and the special joint *F* of *A* was then

sealed on at *C* to the side-tube of the flask *B*, which in turn was provided with a special joint *D*. After the apparatus had been cleaned, the long neck of *B* was connected through the bulb *E* with the pump, and then a piece of glass rod was inserted in the side-tube of the joint *F*; this side-tube and the narrow tube of *D* were sealed, and the whole flask *B* was completely exhausted and sealed off from the pump at *G*. By tilting the apparatus the joint at *F* was broken, and the liquid in *A* was then poured into *B*. Finally, *B* was sealed off from *A* at the capillary *H*.

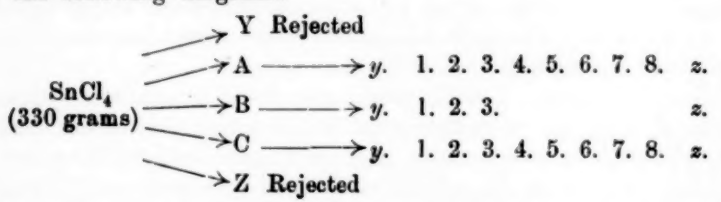
Some fragments of the crystalline hydrate had been carried into the second flask, and the greater part of this slight impurity was next removed by heating the whole flask to 100°, except the bulb *E*, which was kept cool. The sublimate was thus driven into the bulb, which was then sealed off at the capillary *K*.

The contents of the flask *B* were then distilled in a vacuum in a sealed apparatus into five approximately equal fractions, Y, A, B, C, and Z, of which the middle three, A, B, and C, were collected in tubes provided with special joints, whilst fraction Y was collected in a fourth vessel and fraction Z was left in the flask.

Each of the fractions A, B, and C was further distilled, A and C into ten fractions each, of which the middle eight were in each case collected in weighed bulbs, and B into four small fractions and one large end-fraction, of which the second and third small fractions (B 1 and B 2) only were collected in weighed bulbs. That only two small fractions of main fraction B were collected in weighed bulbs was due to the accidental cracking of the apparatus after the third small fraction (B 2) had been sealed off.

These final fractionations of stannic chloride were carried out in a manner quite similar to that of the fractionations of vanadyl trichloride described in a former communication (Briscoe and Little, *loc. cit.*), and need not be further discussed.

The general course of the fractionation in a vacuum is indicated in the following diagram:



It will be seen that nineteen fractions were ultimately obtained in weighed bulbs. The fractions *y* were collected in unweighed bulbs, and the fractions *z* were left in the main vessels.

Of these fractions fifteen were analysed, namely, A 4, A 5, A 6, A 7, A 8, B 1, B 2, and all the eight fractions of main fraction C.

Fraction B 3 was collected after the cracking of the apparatus, and contained a visible amount of the crystalline hydrate; fractions A *y* and A 1 also contained minute but visible traces of this substance, and, consequently, neither A 1 nor A 2 was analysed. The bulb containing fraction A 3 was accidentally broken.

No attempt was made to test the stannic chloride for possible impurities, as these could only be present in amounts so minute as to be entirely beyond the range of sensitiveness of the tests available. The best possible evidence of the purity or otherwise of the stannic chloride is found in a comparison of the results of analyses of fractions so widely separated as A 4 and C 8.

The Solubility of Metastannic Acid in Aqueous Oxalic Acid and Tartaric Acid.

The most serious problem arising in connexion with the direct determination of chlorine in stannic chloride was the rapid hydrolysis of this salt in dilute solution. A solution of the concentration employed in the analyses, that is, containing 1·5—2·0 grams of stannic chloride per litre, deposits considerable amounts of metastannic acid within three days. It is hardly probable that the precipitate would occlude much chloride, but its presence would render it almost impossible to make nephelometric tests owing to the time (over ten days) taken for it to settle.

Investigations have been made on the solubility of metastannic acid in solutions of oxalates, from which it has been concluded that salts of a complex oxalostannic acid are formed. It has also been observed that metastannic acid is soluble in solutions of oxalic acid (Rosenheim and Platsch, *Zeitsch. anorg. Chem.*, 1899, **20**, 281), although the nature of the compound formed is not definitely known. It has been stated that it is possible to obtain the oxalostannic acid in the crystalline form (Péchard, *Compt. rend.*, 1893, **116**, 1513), but this lacks confirmation. There is evidence that similar action takes place with other organic acids, especially with hydroxy-acids (see, for example, Rosenheim and Schnabel, *Ber.*, 1905, **38**, 2777).

It seemed probable, therefore, that by the use of oxalic acid or certain hydroxy-acids it would be possible to keep in solution the metastannic acid produced by the hydrolysis of stannic chloride. From the point of view of the determinations it was necessary that the substance selected should fulfil certain conditions:

(1) It must prevent precipitation for a period of at least a fortnight under the conditions obtaining in the analyses;

(2) It must be obtainable perfectly free from chlorine; and

(3) It must not hinder the complete precipitation of the chlorine as silver chloride.

It seemed likely that oxalic acid and perhaps tartaric acid would fulfil condition (2) satisfactorily. The prevention of the precipitation of chlorine by these reagents could hardly take place unless through the formation of complex ions containing chlorine, of which the investigations referred to above afford no evidence whatever.

It remained, therefore, to ascertain the extent to which oxalic and tartaric acids fulfilled the first requirement. Six solutions were prepared, each containing 1·5 grams per litre of stannic chloride, to which were added various amounts of nitric acid and of oxalic acid or Rochelle salt as stated below. In experiments IV, V, and VI, the concentration of tartaric acid equivalent to the Rochelle salt taken is given in the fifth column, and allowance is made for the nitric acid used in liberating this acid from the salt. The last column shows the time elapsing before a visible opalescence due to precipitated metastannic acid was observed in the liquid.

No. of Test.	Nitric acid. Grams per litre.	Oxalic acid. Grams per litre.	Rochelle salt. Grams per litre.	Tartaric acid. Grams per litre.	Time.
I.	1·0	2·0	—	—	>10 weeks.
II.	1·0	10·0	—	—	>10 weeks.
III.	10·0	10·0	—	—	>10 weeks.
IV.	0·3	—	4·0	2·1	10 days.
V.	5·7	—	14	7·4	30 days.
VI.	11·1	—	20	10·6	45 days.

No precipitation was ever observed in those solutions to which oxalic acid had been added.

The results for Rochelle salt may fairly be said to suggest that the lapse of time before precipitation varies directly as the concentration of tartaric acid, and does not depend on the concentration of the nitric acid within the range covered by these experiments.

It was found that by recrystallisation both oxalic acid and Rochelle salt could be freed completely from chlorides, but, as the experiments above described show clearly that the former substance was to be preferred on account both of the smaller quantity required and the longer time during which precipitation is prevented, Rochelle salt was used for one of the analyses and oxalic acid for the remaining fourteen.

Method of Analysis.

The procedure followed in the analyses of the fractions of stannic chloride was essentially the same as that employed by Richards and

his collaborators in the determination of the ratio of silver to a chloride.

A large bottle of Jena glass provided with a well-fitting stopper was very carefully cleaned. About 2—3 litres of pure water were then introduced, together with 10—30 c.c. of pure nitric acid and 10—30 grams of oxalic acid. In the analysis of fraction C 4 100 grams of Rochelle salt and 110 c.c. of nitric acid were used.

When the solution had become quite clear, the bulb containing the required fraction of stannic chloride was lifted from its box by means of a long, hooked glass rod, and washed externally with pure water and lowered into the bottle. The bottle was then stoppered and shaken in order to break the bulb.

It was found that if the breaking of the bulb were accomplished by shaking the bottle sideways the products of decomposition were apt to escape entire absorption in the solution, as was evidenced by the formation of a fog in the upper part of the bottle. Whilst it is unlikely that any loss of chlorine would thus be caused if the fog were allowed to clear before the bottle was opened, it seemed desirable to eliminate the risk entirely. Accordingly, the bulb was broken by holding the bottle vertical, and giving it a sharp jerk in a vertical direction; this action caused the bulb to strike with some force against the bottom of the bottle while remaining completely submerged in the solution.*

After the bottle had stood for a time, the fragments, and especially the capillary ends, of the bulb were broken with a flat-ended glass rod, which was carefully rinsed in the bottle before it was removed. Finally, the chloride solution was diluted to a bulk of 3—5 litres.

A quantity of pure silver one or two milligrams less than that actually required for the stannic chloride taken was next weighed out and dissolved in an excess of dilute nitric acid, its solution being assisted by warming the flask to about 35°. The solution was then heated to about 80° in order to expel the greater part of the nitrous acid formed, cooled, and diluted to 800—1100 c.c., and finally added to the chloride solution prepared as described above.

In effecting the transference of the silver solution the bottle containing the stannic chloride was shaken steadily with a rotary motion until the solution was itself rotating rapidly. The bottle was then set down, and the silver solution poured steadily into it. The flask which had contained the silver solution was rinsed five to eight times with quantities of 100 c.c. of water, and the rinsings

* This apparently trivial point has been given prominence because it appeared possible that the "accidental" errors in precise work might be attributable to a lack of refinement in the mechanical operations: this question is again referred to in the discussion of the results.

were added to the solution in the bottle. Finally, the small amount of dilute silver solution supposed to be required to bring the total weight of silver to the calculated amount was added from a burette, and the bottle was stoppered, shaken gently, and set aside. After two days the bottle was shaken vigorously on several occasions, and about the sixth or seventh day a nephelometric test was made. Subsequently small quantities of silver or chloride solution were added as required until the end-point was reached.

The type of nephelometer employed and the methods of using it having been dealt with in a former communication (Briscoe and Little, *loc. cit.*) need not be described here.

FIG. 2.

All the analyses were carried out in a small laboratory which was devoted entirely to this work, and was kept permanently dark. Careful precautions were taken to keep the atmosphere of the room free from dust and fumes of hydrochloric acid.

The mixing of the silver and stannic chloride solutions was effected under yellow light, and although some of the bottles were exposed to the light of an ordinary carbon filament lamp during the later stages of the titrations no discoloration of the silver chloride was ever observed.

A New Form of Solution Flask for Silver.

The transference of the silver solution from the flask in which it is prepared to the vessel containing the chloride solution is evidently the chief point of the whole series of operations where accidental loss may take place. In the earlier experiments the flask employed was of the ordinary round type, but was fitted with a stopper carrying a set of bulbs similar to those shown in Fig. 2 (*A*), and the pouring of the liquid was effected in the ordinary way with the aid of a glass rod. This procedure is slow, and imposes considerable strain on the operator.

A new form of solution flask was therefore devised and constructed of Jena glass; its shape will readily be understood on reference to Fig. 2. During the dissolution of the silver the cap *C* closed the side-tube *B*, and the bulbs prevented any loss of silver

by spraying of the solution. When all the silver had dissolved the tube *A* carrying the bulb was rinsed into the flask and removed, the cap *C* was taken off, and the diluted silver nitrate solution was poured out through the side-tube. Then, while the side-tube was kept within the receiving vessel, it was possible to tilt the flask a little back so that a stream of water from a wash-bottle directed into the neck would wash the silver nitrate solution remaining in the upper part of the flask and in the side-tube *B* either back into the bottom of the flask or out through the side-tube. Then the outside of the tube *B* could be washed, and the flask removed without risk of loss of silver. The washings of the flask were performed by the same process.

TABLE II.

Fraction of $SnCl_4$.	Oxalic acid. Sample.	Oxalic acid. Weight used. Grams.	Nitric acid. Sample.	Nitric acid. Volume used. c.c.	Solution flask.*	Volume of solution. c.c.	Duration of analysis. Days.
A.4	II	15	II	20	β	4600	14
A.5	II	15	I	15	β	5900	15
A.6	II	10	II	20	β	6700	20
A.7	II	30	II	30	α	7200	16
A.8	II	20	II	13	β	3500	18
B.1	I	15	I	10	α	5900	47
B.2	I	10	I	10	α	3900	33
C.1	I	12	I	20	α	5600	29
C.2	I	10	I	10	α	4400	30
C.3	II	10	I	10	α	5600	22
C.4	—	— †	II	110	β	5500	36
C.5	I	10	II	15	α	5900	21
C.6	II	35	II	15	β	5900	31
C.7	II	20	II	25	β	5800	19
C.8	I	12	II	10	β	6700	20

* The flask denoted by α is the simpler type, whilst the flask β is the special vessel shown in Fig. 2.

† One hundred grams of Rochelle salt were used in this analysis.

TABLE III.

No. of fraction.	Weight of $SnCl_4$ in vacuum.	Sample of silver.	Weight of silver in vacuum.	Ratio: $SnCl_4/4Ag$.	Atomic weight of tin (Cl = 35·460).	Atomic weight of tin (Cl = 35·457).	Deviations from mean and average errors.
A.4	9·02435	II	14·9475	0·603736	118·685	118·697	−0·002
A.5	9·39855	II	15·5666	0·603764	118·696	118·708	+0·009
A.6	10·32760	IV	17·1058	0·603748	118·689	118·701	+0·002
A.7	9·17005	IV	15·1880	0·603769	118·699	118·711	+0·012
A.8	6·68995	II	11·0808	0·603742	118·686	118·698	−0·001
B.1	9·33130	I	15·4570	0·603694	118·666	118·678	−0·021
B.2	7·77450	I	12·8764	0·603779	118·702	118·714	+0·015

TABLE III (*continued*).

No. of fraction.	Weight of $SnCl_4$ in vacuum.	Sample of silver.	Weight of silver in vacuum.	Ratio: $SnCl_4/4Ag$.	Atomic weight of tin (Cl = 35·460).	Atomic weight of tin (Cl = 35·457).	Deviations from mean and average errors.
C.1	9·22730	II	15·2840	0·603723	118·678	118·690	−0·009
C.2	7·55785	I	12·5183	0·603744	118·688	118·700	+0·001
C.3	9·11535	II	15·0983	0·603732	118·683	118·695	−0·004
C.4	9·22875	II	15·2866	0·603715	118·675	118·687	−0·012
C.5	9·21890	V	15·2696	0·603742	118·686	118·698	−0·001
C.6	11·29055	V	18·7017	0·603715	118·675	118·687	−0·012
C.7	9·89635	III	16·3912	0·603760	118·694	118·706	+0·007
C.8	9·43385	II	15,6250	0·603767	118·696	118·708	+0·009
General means				0·603742	118·686	118·698	0·008
General means, omitting B.1 and B.2				0·603744	118·687	118·699	0·006
Means of Series A				0·603752	118·691	118·703	0·005
Means of Series B				0·603734	118·684	118·696	0·018
Means of Series C				0·603734	118·684	118·696	0·006

The Ratio of Stannic Chloride to Silver.

Of twenty-four fractions of stannic chloride which should have been obtained in weighed bulbs eighteen were actually collected and weighed; of these two were rejected on account of possible contamination with water (A 1 and A 2), and one met with an accident (A 3). The remaining fifteen fractions were analysed in the manner which has been described. The details of the analyses are given in table II, and the results obtained in table III.

The analyses of fractions B 1 and B 2 were of the nature of preliminary determinations, as they were the first to be performed, and in all such investigations as the present the liability to error is unduly great until the technique has been thoroughly mastered.

On examination of table III it will be found that the extreme variation in the values of the ratio $SnCl_4 : 4Ag$ lies between the values for B 1 and B 2, and amounts to 0·000085, or 1 part in 7200, with a corresponding variation in the atomic weight of tin of 0·036 or 1 part in 3300. If the analyses of fractions B 1 and B 2 are omitted from consideration and those of fractions A 4 to A 8 and C 1 to C 8 taken together as the final series of thirteen determinations, the values of the ratio $SnCl_4 : 4Ag$ vary by 0·000054 or 1 part in 11,000, which corresponds with a variation in the value for the atomic weight of 0·024 or 1 part in 4950.

The general mean of all fifteen determinations of the ratio $SnCl_4 : 4Ag$ is 0·603742 with a "probable error" of $4·1 \times 10^{-6}$, and the mean of series A and C only is 0·603744 with the "probable error" $3·5 \times 10^{-6}$.

In view of the fact that the variations of the results of the analyses of B 1 and B 2, from the mean, although larger than the variations in the other analyses, are in opposite directions, it is, perhaps, doubtful whether their rejection is justifiable. It will be seen, however, that in either case the mean value of the ratio $SnCl_4$: 4Ag is practically the same, although the probable error is naturally greater if the extreme values are considered.

In discussing the value to be attached to these results regard must first be had to the purity of the stannic chloride and silver used. For the reasons given in the section on the preparation of stannic chloride there seems to be little doubt that the material was obtained free from chlorides of other elements. The action of a small quantity of water on a large excess of stannic chloride does not produce hydrogen chloride, but the solid hydrate of stannic chloride previously referred to, and there is good reason to believe that all traces of this hydrate were eliminated by the processes of decantation and fractionation described.

Supposing that a small amount of hydrogen chloride had been formed it is conceivable that a mixture of this substance with stannic chloride, of constant boiling point, might have resulted, but it seems improbable that the hydrogen chloride could have continued to exist in the presence of the metallic tin used in the first distillation in a vacuum. Moreover, in the distillation of main fraction A the earlier fractions, A x—A 5, were condensed at the temperature of liquid air, whilst the later fractions, A 6—A 8, were cooled only to $-10°$; and the attendant variation in pressure within the apparatus should have had an effect on the composition of the distillate if a mixture were being distilled.

Another possibility is that the vapour of stannic chloride might undergo partial dissociation into stannous chloride and chlorine. The evidence that no such dissociation occurred is (1) that the reduction of stannic chloride to stannous chloride even by hydrogen does not take place to an appreciable extent below 200° (Meyer and Kerstein, *Ber.*, 1913, **46**, 2882); (2) that the distillations were always carried out at temperatures below 30°; and (3) that when the final main fraction Y was evaporated to dryness in a vacuum there was no visible residue of stannous chloride.

No systematic variation can be observed in the values of the ratio of stannic chloride to silver, but, on the contrary, the composition of the earlier fractions of series A is substantially the same as that of the later fractions of series C. This fact appears to indicate clearly that any impurity which may have been present in the stannic chloride formed so small a proportion of the whole

as to produce an effect on the results which is negligible in comparison with the experimental error.

With regard to the silver a similar argument may be advanced to show that the variation in the amount of impurity present in the five different samples employed must have produced effects on the atomic weight small in comparison with the errors of experiment. These samples of silver were prepared by two different methods, in the one case with variations in the details of procedure, and the agreement of the results, therefore, affords strong presumptive evidence of the substantial purity of all the samples. A further indication of this is afforded by comparative assays made at the Royal Mint, which show that both the methods employed for the purification of the silver are capable of yielding a product which is 999·97—999·98 fine as compared with the purest sample of silver at the Mint taken as 1000 fine. The effect of any impurity in the silver would be to cause the atomic weight deduced to be lower than the true value.

In addition to impurity in the stannic chloride or silver the following possible sources of error in the determination of the ratio $SnCl_4 : 4Ag$ have to be considered:

(1) Presence of chloride in the reagents (water, nitric acid, oxalic acid, Rochelle salt) used in the titrations.

(2) Mechanical loss of silver in transference.

(3) Co-precipitation of silver oxalate or tartrate with silver chloride.

(4) Mechanical loss of chloride during the titration.

(5) Occlusion of soluble chloride by precipitated silver chloride.

(6) Prevention of complete precipitation of chlorine as silver chloride owing to formation of complex ions containing chlorine.

Errors due to causes (1), (2), or (3) would make the apparent value of the atomic weight less, whilst those due to causes (4), (5), or (6) would make it greater than the true value.

The precautions taken in the purification of the reagents and the negative results of tests for chlorine in them render it improbable that the error due to (1) is appreciable. With regard to (2) an attempt was made to ascertain whether loss of silver occurred in the process of transference by the use of the new form of solution flask described, but the change in procedure had no appreciable effect on the results.* Supposing co-precipitation of silver oxalate

* In this operation and in the breaking of the bulbs (p. 77) the methods of manipulation were varied in the course of the analyses with a view to ascertaining whether the "accidental errors" of the determinations could be traced to loss or gain of silver or chlorine through lack of refinement in the manual details. The results clearly lead to the inference that such errors cannot be attributed to this source. That such variations are due to errors of weighing is highly improbable;

or tartrate with silver chloride (3) to take place, the amount of silver thus lost to the titration would, presumably, decrease as the concentration of nitric acid was increased, but no such effect is apparent in the data. Further, the agreement of the result of the analysis of fraction C 4, in which tartaric acid was used, with the other results suggests that no perceptible error is due to this cause.

All possible care was taken to prevent mechanical loss of chloride during the analyses (see p. 77), and it is evident that such a source of error as (4) cannot otherwise be eliminated. In reference to (5), it seems reasonable to assume that any occlusion of silver or chlorine by the precipitate was inconsiderable, as variations in the duration of the analyses (between fourteen and forty-seven days) and in the concentration of the solutions do not appear to have any influence on the result. Baxter and Moore, in the course of analyses of phosphorus trichloride (*J. Amer. Chem. Soc.*, 1912, **34**, 1644), have shown that occlusion produces an error which is at most 1 part in 35,000, and is much reduced when the duration of the analyses is, as in the present case, fourteen days or more.

The consideration of the probable magnitude of the uncertainty in the results due to (6) presents difficulties owing to the lack of knowledge of the precise manner in which oxalic and tartaric acids act in retaining metastannic acid in solution. There does not appear to be in the literature any evidence for the formation of complex ions containing chlorine (see p. 76), and, moreover, were such complexes formed, the amount of chlorine thus retained would certainly depend in some way on the concentration of the organic acid. That a large variation in the amount of oxalic acid used produced no corresponding variation in the ratio of stannic chloride to silver is, therefore, good evidence that the chlorine was always completely precipitated. Again, the proportion of chlorine present in a non-precipitable form would very probably vary with the acid used, but no such effect is to be observed on comparison of the analysis of fraction C 4 with the others.

Criticism may possibly be directed to the fact that no analyses were made by the gravimetric measurement of the ratio $SnCl_4 : 4AgCl$. It has, however, been shown repeatedly that the titration with silver and the weighing of silver chloride give identical results when applied to the same material.*

they must, therefore, as Richards has suggested, be mainly due to impurities in the reagents or to irregularities in the course of the chemical reactions involved in the analyses.

* For determinations in which the two methods were applied together to a series of experiments see Richards and Archibald, *Proc. Amer. Acad.*, 1903, **38**, 443; Archibald, T., 1904, **85**, 786; Baxter and Coffin, *Zeitsch. anorg. Chem.*, 1906, **51**, 171; Baxter and Hines, *J. Amer. Chem. Soc.*, 1906, **28**, 1560. For the application

As the gravi-volumetric method involves much simpler manipulation, and is therefore less liable to error, it seemed preferable to adopt it entirely. Moreover, the performance of the gravimetric analyses almost necessitates the co-operation of two persons, as it is difficult for one alone to carry out with certainty such operations as the filtration of large volumes of liquid through Gooch crucibles.

The antecedent data involved in the calculation of the atomic weight of tin from the values of the ratio $SnCl_4 : 4Ag$ are the atomic weights of silver and chlorine, for which the values 107·88 and 35·46 respectively are adopted by the International Commission. Probably the numbers Ag = 107·880 and Cl = 35·457 determined by Richards and his collaborators represent more nearly the ratio between these atomic weights, although, in the light of recent investigations, it would seem that the true value of silver in reference to O = 16·00 is probably slightly below, rather than above, 117·880.

If the values Ag = 107·880 and Cl = 35·457 are used, the atomic weight of tin deduced is about 0·012 higher than that obtained by taking Cl = 35·46.

In table III are given the mean values of the atomic weight of tin deduced from determinations of the ratio SnCl : 4Ag; it will be seen that the mean of the fifteen determinations is 118·69 or 118·70, according to the value adopted for the atomic weight of chlorine. The "average error" † of the values of the atomic weights from which each mean is deduced is given in the last column opposite that mean. The "probable error" of the value Sn = 118·698 (Cl = 35·457) deduced from all determinations is 0·0013, whilst that of the value Sn = 118·699 obtained by omitting the analyses of B 1 and B 2 is 0·0011.*

Taking into consideration the possible sources of error in the determinations it is clear that the most probable value of the atomic weight of tin is **118·70**. On the basis of the experiments now under discussion it does not seem likely that the true value of the atomic weight will differ by more than 0·01 from this value.

of the two methods separately in different series of experiments, see, for example, Thorpe, *Ber.*, 1880, **16**, 3014; Richards and Stachler, *Pub. Carnegie Inst. Washington*, 1907, No. **69**, 7; Richards and Wells, *ibid.*, 1905, No. **28**, 52; Baxter, Hines, and Frevert, *J. Amer. Chem. Soc.*, 1906, **28**, 770; Richards and Hönigschmid, *ibid.*, 1911, **33**, 28.

* In the general statement of the results of this and earlier determinations the author has given in all cases the average error of the means, and not the "probable error," as the former is a more useful standard of comparison when the relative accuracy of the individual observations in different series is under consideration. At the same time, in accordance with custom, the "probable error" is also given in certain cases.

TABLE IV.

Ratio measured.	Error in the atomic weight of tin produced by an error of 1 in 1000 of the ratio.
$Sn : SnO_2$	0·56
$Sn : 2BaSO_4$	0·053
$Sn : (NH_4)_2SnCl_6$ ...	0·174
$Sn : K_2SnCl_6$	0·129
$Sn : SnBr_4$	0·162
$SnCl_4 : 4Ag$	0·25

In estimating the weight attaching to this result it is necessary to consider in what way, if any, the earlier determinations are unsatisfactory. The discordance in the values 1—7 and 11 in table I clearly suggests that the oxidation of tin with nitric acid is capable, even in the hands of the most experienced analysts, of giving very variable results. The best determinations of the ratio $Sn : SnO_2$ by oxidation (Nos. 4 and 5), in which attempts were made to ascertain and to avoid the chief errors, give values agreeing with those obtained by the reduction of stannic oxide in hydrogen, but if the results are considered in relation to those obtained by Bongartz and Classen, they suggest that stannic oxide is not a suitable compound to employ in atomic-weight determinations, a conclusion the correctness of which seems inherently probable from the general character of that substance.

From table IV, in which is given the error produced in the atomic weight of tin by an error of 1 part in 1000 in the determination of each of the ratios here dealt with, it will be seen that the measurement of the ratio $Sn : SnO_2$ is, on this ground also, open to serious objection.

The results obtained by Bongartz and Classen cannot be so easily accounted for. Whilst the nature of some of the compounds weighed (ammonium and potassium stannichlorides) and the methods of analysis employed (for example, in the determination of the ratio $Sn : 2BaSO_4$) are not in accordance with modern standards, the results obtained in the different series of determinations are fairly concordant. One very serious criticism of their investigation that can be made is that the tin was in every case weighed as an electrolytic deposit on platinum, and that this tin had been deposited from a solution containing a number of different compounds in solution, and was dried only by washing with alcohol and heating to 100°. It has been shown that electrolytically deposited silver contains included material amounting to about 0·02 per cent., which is not expelled by heating to any temperature short of the softening point of the metal (Richards and Heimrod, *Proc. Amer. Acad.*, 1902, **37**, 415; compare Smith, Mather, and Lowry, *Phil. Trans.*, 1908, [*A*], **207**, 545; Richards, *Proc. Amer.*

Acad., 1908, **44**, 91). Moreover, it has been found that, even in such a simple case as the electrolysis of silver nitrate solutions, side-reactions occur; in the deposition of tin such side-reactions might seriously affect the composition of the deposit. It is, therefore, not improbable that metallic tin, deposited from an electrolyte of complex composition, may have contained included solution or gas sufficient to affect its weight to a serious extent, and it does not appear that any steps were taken to ascertain whether the tin was impure from this cause. Assuming that such inclusion of impurity occurred, the weight of metal found would be greater than its true weight, and the atomic weight deduced from determinations affected by this error would be higher than the true value. It is worthy of note that in the case where the composition of the electrolyte was simplest, namely, the analysis of stannic bromide, the result obtained was lower than the other results by 0·1, a quantity greater than the average error of any single series of their determinations except the first.

The true value of this atomic weight cannot, of course, be fixed by any one series of determinations, and further work on the subject is much to be desired. The result here given is not improbable, in that it lies within the range of earlier values. It has, it is true, been arrived at by the determination of a single ratio, but the analytical methods involved have repeatedly been shown to be capable of yielding results of the highest degree of accuracy. All the variable factors in the analyses have been varied over a comparatively wide range, notwithstanding which fact the results all lie between 118·678 and 118·714, and eleven of the fifteen between 118·690 and 118·711. The atomic weight finally deduced, **Sn = 118·70**, would seem to be worthy of considerable confidence.

In conclusion, the author desires to express his thanks to Professor H. Brereton Baker for the numerous facilities he has so kindly afforded for the prosecution of this investigation.

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IX.—*Colorations Produced by Some Organic Nitro-compounds with Special Reference to Tetranitromethane.*

By Ernest Magowan Harper and Alexander Killen Macbeth.

In a recent paper (P., 1913, **29**, 161) Clarke, Macbeth, and Stewart extended the observations of Ostromisslenski (*J. pr. Chem.*, 1911, [ii], **84**, 489), and showed that the production of colour in the case of tetranitromethane was not limited to the influence of ethylenic compounds; the phenomenon is of more general occcrrence, and, as a rule, a substance containing an atom which can exercise a higher degree of valency gives a colour on the addition of tetranitromethane.

As the phenomenon is primarily a colour reaction it seemed most reasonable to approach it along the line of absorption spectroscopy, and such an investigation was undertaken by us. The absorption of the influencing substance was obtained, and from it the strength of solution which would be fairly diactinic was found. Tetranitromethane was photographed in an alcoholic solution of the influencing substance of a suitable constant strength, and the effect on the absorption of tetranitromethane was thus recorded.

Tetranitromethane itself gives no colour in dry alcohol. With an influencing substance a yellow colour is produced on mixing the solution, but the absorption spectrum is found to differ only very slightly from that of the nitro-compound alone. The colour, however, deepens on keeping, and after some time the spectrum shows a great change; the absorption becomes strongly selective, and a band appears at the region $1/\lambda$ 2800—$1/\lambda$ 2900. The penetration of the band increases as time goes on, and finally attains a maximum. This can be seen from a study of the figures given.

Carvene, allyl alcohol, and β-methyl-Δ^{β}-butylene (trimethylethylene) were taken as representatives of substances containing the ethylene linking. The results are expressed in Fig. 1. The increase of the penetration of the band is clearly seen in the cases of carvene and β-methyl-Δ^{β}-butylene.

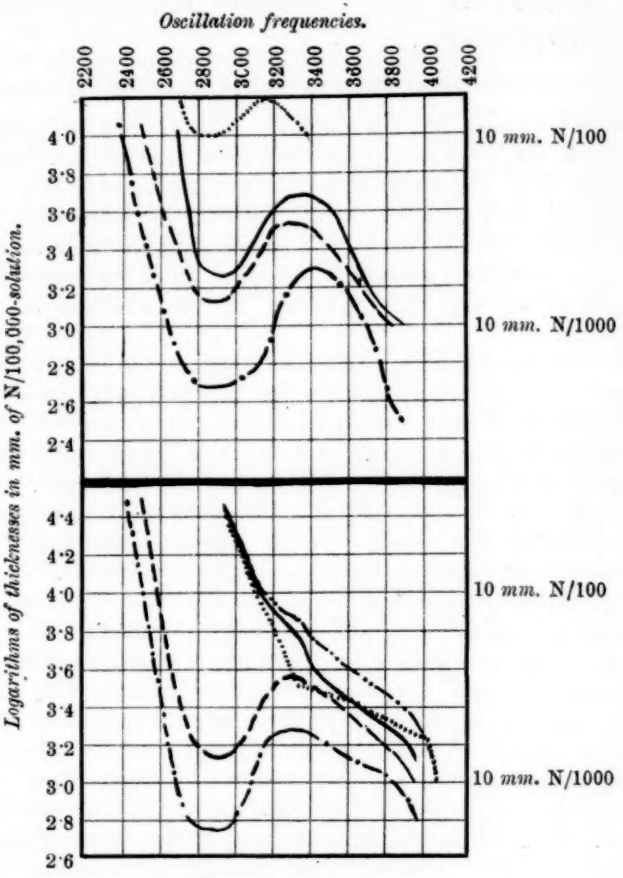
The substances containing bivalent sulphur atoms, which were studied, were ethyl, propyl, allyl, and pentamethylene sulphides; also 1:4-thioxan and ethyl mercaptan. The results obtained in typical cases are expressed in Fig. 2.

Amino-compounds were also used as influencing substances, and the curves are given in Fig. 2.

From a study of the curves it is seen that the general effect

obtained on mixing tetranitromethane and a substance containing an ethylene linking, or an atom capable of exercising higher valency,

FIG. 1.



Upper curves.

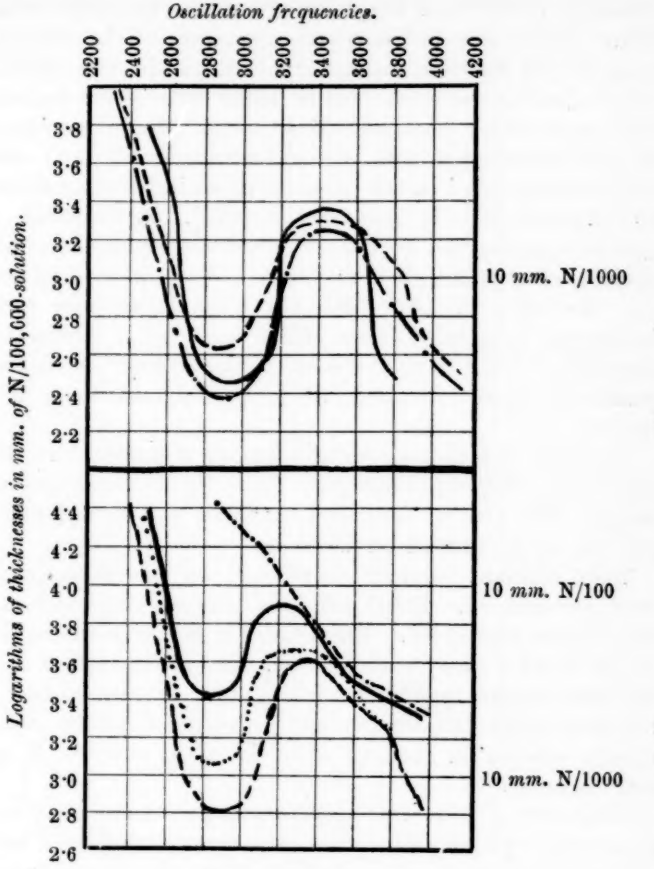
..... *Tetranitromethane* + N/10-*allyl alcohol* (*after* 14 *days*).
——— *Tetranitromethane* + N/10-*carvene* (*after* 4 *hours*).
— — — — ,, ,, ,, (*after* 3 *days*).
— · — · — ,, ,, ,, (*after* 14 *days*).

Lower curves.

——— *Tetranitromethane* + N/10-*amylene* (*after hydrogen chloride*).
— — — — ,, ,, ,, (*after* 5 *days*).
— · — · — ,, ,, ,, (*after* 14 *days*).
—··—··— ,, ,, ,, (*after mixing*).
..... *Nitroform.*

is the development of strong selective absorption with a maximum at, or about, $1/\lambda$ 2850.

FIG. 2.



Upper curves.

——— *Tetranitromethane* + N/10-*ethyl mercaptan* (*after* 15 *minutes*).
(*after* 4 *hours*).

– – – – *Tetranitromethane* + N/10-*methylamine* (*after* 15 *minutes*).
(*after* 30 *minutes*).

– · – · – { *Tetranitromethane* + N/10-*diethylamine* (15 *minutes*).
{ *Tetranitromethane* + N/10-*triethylamine* (15 *minutes*).

Lower curves.

——— *Tetranitromethane* + N/10-*pentamethylene sulphide* (*after* 2 *days*).

– – – – ,, ,, ,, ,, (*after* 5 *days*).

– · – · – ,, ,, ,, ,, (*after mixing*).

. . . . . *Tetranitromethane* + N/10-*propyl sulphide* (*after* 5 *days*).

In searching for the explanation of these colorations it seemed advisable to examine other simple nitro-compounds. Substances containing one nitro-group (nitromethane, etc.) were tried, but with

negative results, no change in the absorption being observed. It appeared likely that the nitro-group in tetranitromethane was influenced by the electronegative character of the other three. To approximate to this molecular condition in the mononitro-compounds, substances were tried in which some of the hydrogen atoms were replaced by electronegative atoms. Monochloronitromethane, monobromonitromethane, dibromonitromethane, and chloropicrin were photographed in the presence of an influencing substance, but no development of a band was observed. It appeared of interest now to examine the behaviour of another type of mononitro-compounds, namely, the alkyl nitrites. Colours were obtained (Harper and Macbeth, P., 1914, **30**, 15) when these were treated with substances containing unsaturated centres or atoms capable of exercising additional valency. The tints developed closely resembled those obtained when tetranitromethane is similarly treated.

Amylene and carvene were taken as representative of the class containing ethylene linkings. These give faint, greenish-yellow colours with propyl, *iso*propyl, *iso*amyl, and benzyl nitrites. The colours are intensified on warming.

With bivalent sulphur compounds the colorations obtained are very pronounced. Ethyl sulphide gives a deep red colour with the nitrites mentioned. Ethyl mercaptan yields similar results, the colour being slightly more intense. The production of colour is not confined to the organic sulphides, but is also shown by some inorganic sulphides—sodium and potassium sulphides giving decided orange colours on shaking with the alkyl nitrites or with tetranitromethane.

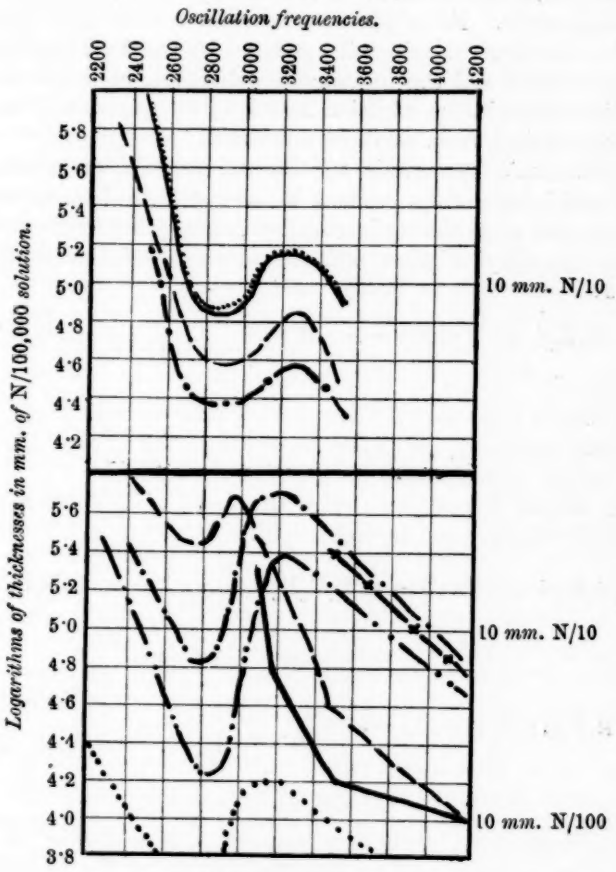
Amino-compounds were also investigated, and yield the characteristic reddish-yellow and orange colours on mixing with the nitrites.

The above cases of colorations were also investigated spectroscopically. The curves are shown in Fig. 3. It will be noticed that all the nitrites examined have practically the same absorption. All the curves showing a strong selective effect with a maximum at an approximate frequency of 2850.

The absorption spectrum of ethyl nitrite and ethyl mercaptan immediately after mixing does not differ appreciably from that of the nitrite itself; after some time (twenty hours) the colour of the solution deepens, and the penetration of the band increases; the general absorption extends further into the visible, and thus produces the change in colour. Similar effects were noticed with the other nitrites. The case of the amines has also been studied, but the increase in the penetration of the band is here not nearly so great.

From the foregoing it is evident that the question of the tetranitromethane colorations is closely allied to the behaviour of the

FIG. 3.



Upper curves.

———— *Ethyl nitrite.*
— · — · — *Ethyl nitrite* + N/10-*ethyl mercaptan* (*after* 60 *hours*).
— — — — *Amyl nitrite* + ,, ,, (*after* 14 *hours*).
· · · · · · · · *Piperidinium nitrite.*

Lower curves.

———— *Phenyldinitromethane in* $CHCl_3$.
— — — — ,, ,, C_2H_6O.
· · · · · · · · K *salt of same in* H_2O.
— · — · — *Bromodinitromethane in* H_2O + 1 *mol.* HCl.
— ·· — ·· — ,, ,, H_2O.

alkyl nitrites; so that if it is proposed to account for the former by the behaviour of the latter a clear understanding of the

processes involved in the latter is essential. A plausible explanation of the latter is here advanced. The spectroscopic results point to the formation of additive compounds of the nitrites and the other substances, the alteration of the absorption on keeping being due to such cause. From the spectroscopic results it is impossible to decide whether the colour is produced by the final additive product of the nitrite and the influencing substance, or is due to an intermediate stage in the addition reaction; the question must therefore be approached from another direction.

Vorländer's hypothesis to account for the formation of the coloured intermediate product in the reaction of an $\alpha\beta$-unsaturated ketone and an acid may be recalled and applied to the present case. With the alkyl nitrites and the bivalent sulphur compounds we have:

$$R_1R_2S + R{\cdot}ONO \longrightarrow \underset{\text{(I.)}}{R_1R_2S\left[\begin{matrix}R\\ \dot{O}NO\end{matrix}\right]} \longrightarrow \underset{\text{(II.)}}{R_1R_2S{<}\begin{matrix}R\\ ONO\end{matrix}}$$

Formula I represents the coloured intermediate product which is quickly produced, and passes slowly into the true additive product II, which is colourless.

A similar hypothesis covers the cases of the amino-compounds and the unsaturated hydrocarbons.

$$R_1R_2R_3N + R{\cdot}ONO \longrightarrow \underset{\text{(I.)}}{R_1R_2R_3N\left[\begin{matrix}R\\ \dot{O}NO\end{matrix}\right]} \longrightarrow \underset{\text{(II.)}}{R_1R_2R_3N{<}\begin{matrix}R\\ ONO\end{matrix}}$$

Coloured, quickly produced.

$$CHR_1{:}CHR_2 + R{\cdot}ONO \longrightarrow \underset{\text{(I.)}}{\begin{matrix}CHR_1{\cdot}CHR_2\\ [R{\cdot}ONO]\end{matrix}} \longrightarrow \underset{\text{(II.)}}{\begin{matrix}CHR_1(ONO){\cdot}CHRR_2\\ \text{or}\\ CHRR_1{\cdot}CHR_2{\cdot}ONO\end{matrix}}$$

Coloured, quickly produced.

If Vorländer's theory is applied the existence of the final additive product must be accepted; proof of the isolation of such compound must therefore be forthcoming. Rây and Rakshit (T., 1911, **99**, 1016, 1470) and Rây and Datta (*ibid.*, 1475) have prepared the additive products of nitrous acid and the alkyl nitrites with primary, secondary, and tertiary amines. Such compounds are all colourless, or, at most, weakly-coloured compounds. Neogi (T., 1911, **99**, 1598) has obtained additive products of cyclic compounds containing tertiary nitrogen with the nitrites. With few exceptions these are colourless compounds. The isolation of the final additive products of the nitrites with bivalent sulphur compounds has been undertaken by us. The existence of the final additive product of the nitrites is thus established, and the applica-

tion of Vorländer's hypothesis to cover the cases of nitrite colorations is therefore justified. The coloured substances obtained by Neogi (pyridine methonitrite, etc.) are evidently cases where the substance has been isolated in the intermediate stage only.

Ostromisslenski (*J. pr. Chem.*, 1911, [ii], **84**, 495) advanced several formulæ to account for the phenomenon observed. The "tetranitromethanates" had a constitution which was one of five indicated, only one nitro-group being involved. Considerable doubt is thrown on the validity of his assumption by our study of the mononitro-compounds where no effect whatever is obtained when such substances are used instead of tetranitromethane. The only case observed where colorations are obtained with a molecule containing one nitro-group is that of the alkyl nitrites. None of the formulæ advanced by Ostromisslenski appears to cover this case.

The question of the colorations produced by tetranitromethane seems to us to be answered from the data we have obtained. One must first postulate an isomerisation of one, or more, of the nitro-groups of the tetranitromethane to a nitrite form. This is induced by the influencing substance used. We have then an intermediate additive product formed as in the case of the nitrites, such compound being the result of the potential of the unsaturated compound, or the atom capable of higher valency. This isomerisation is not an extravagant demand, and affords a very simple explanation of the observed facts. The first fact that warrants this assumption is the similarity of the colorations obtained in the cases of tetranitromethane and the alkyl nitrites. The curves show clearly the parallel between the nitrites and tetranitromethane. The characteristic nitrite band has a maximum at an approximate frequency of 2850, and it is noteworthy that all the curves obtained by the interaction of tetranitromethane and widely differing compounds containing centres of residual affinity develop this same band. It therefore seems justifiable to postulate that such isomerisation does occur. The isomerised nitrite group need not be chemically identical with the ordinary nitrite group.

Hantzsch and Voigt (*Ber.*, 1912, **45**, 85), from a spectroscopic study of many nitro-compounds and their salts, classified these compounds under three types, namely, (*a*) the true nitro-group, (*b*) the *aci*-nitro-group, and (*c*) the conjugated *aci*-nitro-group. The absorption spectra obtained with tetranitromethane closely resemble the particular case of Hantzsch's conjugated *aci*-type when the compounds contain two or more nitro-groups attached to the same carbon atom. The application of this hypothesis to the case of tetranitromethane might therefore appear likely. Such application must first postulate the decomposition of the tetranitromethane to

nitroform in order to supply the necessary wandering hydrogen atom. The application of the conjugated *aci*-nitro-hypothesis therefore involves an assumption as great as, if not greater than, that demanded by the nitrite isomerisation hypothesis. Moreover, the necessary experimental confirmatory evidence is wanting. Ostromisslenski (*loc. cit.*) showed that colours can be obtained with nitroform, but these are not nearly so intense as those obtained when tetranitromethane is used. If the coloration depends on the conjugated *aci*-form of nitroform it is reasonable to expect that it will be more intense when nitroform itself is used than when the decomposition of tetranitromethane is depended on for the supply of nitroform.

It has been shown (Fig. 1) that tetranitromethane and amylene give a band on keeping for ten days. After treatment with dry hydrogen chloride this band disappears, and the absorption spectrum is found to be practically identical with that of tetranitromethane. It is therefore not reasonable to suppose that the colours are a result of the decomposition of tetranitromethane. Direct estimations of the amount of nitro-compound present in the solutions are now being made, and will form the subject of a further communication.

Examination of the curves attributed by Hantzsch and Voigt (*loc. cit.*) to the conjugated *aci*-nitro-compound shows that they are of widely differing nature, having maxima at different positions extending over the photographic range. The only uniformity in the curves is noticed in the case of those compounds which have two or more nitro-groups attached to the same carbon atom, and a wandering hydrogen atom. The salts of all these have maxima at $1/\lambda$ 2850. The same band is also found in their aqueous solutions. It would appear that the hypothesis of a conjugated *aci*-nitro-group could be rejected in these cases, and the observation accounted for by the nitrite isomerisation. To meet the cases of dinitro-compounds which contain no wandering hydrogen atom, and develop no selective absorption, we are driven to the assumption that a labile hydrogen atom has an influencing effect on the isomerisation in question.

Baly and Rice (T., 1913, **103**, 2085) examined the absorption of trinitrophenol, trinitroanisole, and trinitrobenzene under different conditions. Two modifications of trinitroanisole in alcoholic solution are noted. The colourless form changes to a yellow variety on exposure to sunlight, and the latter shows a selective effect with a maximum in the region 350 $\mu\mu$ ($1/\lambda$ 2860). These modifications cannot be accounted for by Hantzsch's hypothesis of a conjugated *aci*-nitro-group. Baly and Rice advance an hypothesis to explain

this phenomenon, and regard it as the first stage in the opening up of the force fields of the nitro-compound by the solvent. It would appear that the instance quoted may be regarded as a confirmation of the nitrite isomerisation hypothesis.

Baly and Rice (*loc. cit.*) suggested that the colours observed by us are due to similar causes, and are instances of "the opening up of the closed system of the complex nitro-compound by the force lines due to the various residual affinities with which it is treated."

Their theory would cover the cases of the polynitro-compounds containing a labile hydrogen which develop a selective effect in aqueous or in sodium ethoxide solution, observed by Hantzsch (*loc. cit.*) and Hedley (*Ber.*, 1905, **36**, 1195, Fig. 3). Here alkali facilitates the opening up, and acid inhibits it. A similar effect is observed in the case of tetranitromethane, an alcoholic solution of which in the presence of $N/10$-sodium ethoxide shows a band with maximum absorption at $1/\lambda$ 2850, the head of the band being at 21 (log thickness in mm. of $N/100{,}000$-solution). The hypothesis has the same weakness as the nitrite isomerisation hypothesis, which necessitates the assumption of the influence of the labile hydrogen atom to cover cases of the nitro-compounds which have no such atom and do not develop a selective effect.

If it is granted that the first stage in the opening up of the nitro-compound is tantamount to the formation of a grouping akin to the nitritic structure it is evident that Baly and Rice's theory can be brought into conformity with our hypothesis.

Summary.

(1) The colorations produced by tetranitromethane when influenced by unsaturated substances or compounds containing an atom capable of exercising a higher valency were spectroscopically investigated. A resultant selective absorption was noted in all the cases examined, with a maximum at $1/\lambda$ 2850 and penetration depending on the time elapsed since mixing.

(2) The colours of the alkyl nitrites when treated with the same influencing substances are found to bear a close relation to the coloration produced with tetranitromethane. The nitrites themselves have selective absorption at $1/\lambda$ 2850. An increase of penetration occurs on keeping the mixtures of the nitrites and influencing solvents.

(3) An hypothesis to account for the tetranitromethane colorations is considered. This calls for the isomerisation of one, or more, of the nitro-groups of the nitro-compound to a structure similar to the nitritic form. The colours are then regarded as parallel to those obtained with the alkyl nitrites, whether these are due to

Vorländer's intermediate compound or not. The isomerised "nitrite" group need not be chemically identical with the ordinary nitrite group. Such isomerisation occurs in other cases when a large number of nitro-groups are attached to the same carbon, and also when a labile hydrogen is attached to the carbon along with two or more nitro-groups.

(4) Baly and Rice's "opening up" theory may be brought into conformity with the views of the authors if the first stage in such opening up of nitro-compounds may be regarded as equivalent to the formation of a structure akin to the nitritic form.

In conclusion, we wish to express our best thanks to Professor Letts and Dr. A. W. Stewart for the interest they have taken in this work and the advice they have given throughout its course.

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X.—*The Optical Rotatory Power of Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts. Part II.*

By GEORGE WILLIAM CLOUGH.

A STUDY of the rotatory powers of tartaric acid and of its methyl and ethyl esters in aqueous solution and in aqueous solutions of sodium and barium haloids has shown that these haloids exert a similar effect on the rotatory powers of the optically active compounds in question (Part I, T., 1914, **105**, 49). The specific rotatory powers of these substances in aqueous solution increase with dilution, but are considerably diminished (or reversed in sign) by the dissolution of sodium or barium haloids. The investigation has now been extended to other optically active derivatives of succinic acid.

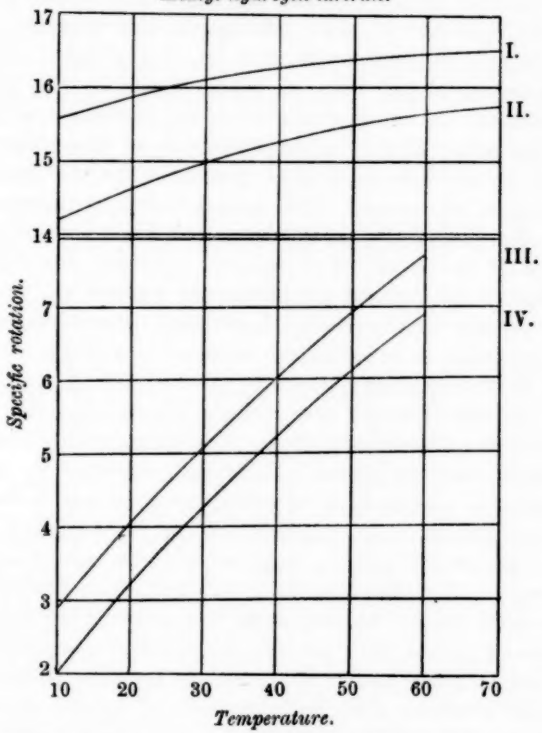
The rotatory powers of methyl hydrogen *d*-tartrate and of sodium hydrogen *d*-tartrate have been determined at various temperatures in aqueous solution and in aqueous sodium chloride. Methyl hydrogen tartrate in aqueous solution is dextrorotatory, and the specific rotation is increased by dilution or by rise of temperature. The expectation that the presence of sodium chloride in the aqueous solution would depress the rotatory power of the ester was realised. The acid ester further resembles tartaric

acid and the neutral methyl ester in that it exhibits lævorotation in a concentrated solution of barium bromide. The curves for methyl hydrogen tartrate (Fig. 1) thus bear considerable resemblance to those for tartaric acid (*loc. cit.*, p. 51).

The influence of temperature and concentration on the rotatory power of sodium hydrogen tartrate in aqueous solution has been

FIG. 1.

Methyl hydrogen tartrate.



I. *Water* (p=9·68). III. *Aqueous sodium chloride* (p=7·65).
II. ,, (p=19·67). IV. ,, ,, ,, p=16·25).

The aqueous sodium chloride contains 5·85 grams of sodium chloride in 20 grams of water.

investigated by Thomsen (*J. pr. Chem.*, 1886, [ii], **34**, 83) and by Grossmann and Wieneke (*Zeitsch. physikal. Chem.*, 1906, **54**, 395). The values obtained by these authors indicate that the rotatory power of this salt is slightly greater in concentrated than in dilute solution. Grossmann and Wieneke further ascertained that the specific rotation reaches a maximum value at 50°. In the present paper are recorded measurements of the rotatory power of sodium

hydrogen tartrate in water and in aqueous sodium chloride at various temperatures for the three wave-lengths mercury-green, mercury-yellow, and sodium-yellow. The specific rotation in aqueous solution appears to be practically independent of the concentration of the solution, although the values obtained for the most concentrated solution ($p=13{\cdot}04$) are slightly higher than those for the other solutions examined ($p=1{\cdot}96$ to $9{\cdot}09$).

The influence of temperature is also the same for all the solutions; the specific rotatory power attains a maximum value, which is constant from 40° to 70°. Although the rotatory power of sodium hydrogen tartrate appears to be, if anything, very slightly greater in concentrated than in dilute solution, the presence of sodium chloride in an aqueous solution depresses the rotatory power of the salt. The relative depression of the rotatory power is, however, much less than that produced by the same salt on tartaric acid or its esters. The optical rotatory dispersive ratios appear to be practically independent of the concentration and temperature of the solutions of sodium hydrogen tartrate.

The influence of sodium or potassium haloids on the rotatory powers of tartaric acid, methyl and ethyl tartrates, and sodium hydrogen tartrate is in striking contrast with the influence of these salts on the rotatory powers of normal sodium and potassium tartrates. At the ordinary temperature, increase in the concentration of aqueous potassium tartrate is accompanied by an increase in the specific rotatory power of the salt, whereas in the case of sodium tartrate, increase of concentration causes a lowering of the rotatory power. It is therefore to be expected that the presence of potassium salts in aqueous solution would increase the rotatory power of potassium tartrate, but that the rotation of sodium tartrate would be depressed by addition of sodium salts. Schütt actually found that potassium chloride in aqueous solution increased the rotatory power of potassium tartrate (*Ber.*, 1888, **21**, 2589), whilst Thomsen observed that sodium nitrate depressed the rotatory power of sodium tartrate (*J. pr. Chem.*, 1886, [ii], **34**, 83). Moreover, Long ascertained that whereas potassium salts caused an increase, sodium salts caused a decrease, in the specific rotation of sodium potassium tartrate in aqueous solution, results in accordance with the fact that potassium tartrate exhibits greater rotatory power than sodium tartrate in aqueous solution (*Amer. J. Sci.*, 1888, [iii], **36**, 351).

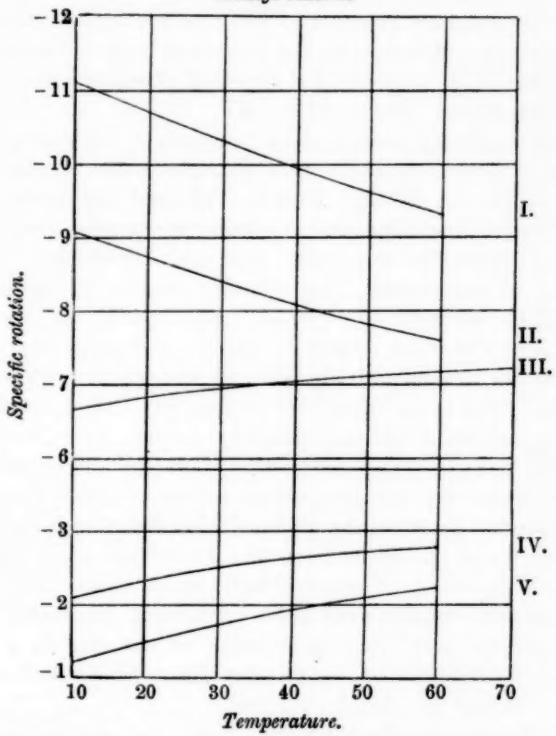
The rotatory power of malic acid at a constant temperature in aqueous solutions of inorganic salts has been fully investigated by Stubbs (T., 1911, **99**, 2265). For the sake of comparison with the values obtained for tartaric acid, the influence of temperature

has now been noted, and the close relationship existing between the rotatory powers of tartaric and malic acids has been confirmed.

The similarity extends to the esters of these acids. The lævorotation of methyl malate increases slightly with rise of temperature during the interval examined (15° to 100°). The temperature-rotation curve (Fig. 2) indicates that the temperature-

FIG. 2.

Methyl malate.



I. *Water* ($p=9{\cdot}73$). III. *Methyl malate.*
II. ,, ($p=50{\cdot}0$). IV. *Aqueous sodium chloride* ($p=7{\cdot}91$).
V. *Aqueous sodium chloride* ($p=43{\cdot}6$).

The aqueous sodium chloride contains 5·85 grams of sodium chloride in 50 grams of water.

coefficient is much less for methyl malate than for methyl and ethyl tartrates. The magnitude of the rotatory power of methyl malate at the ordinary temperature is greater in aqueous solution than in the pure state, and increases with dilution of the solution. The temperature-coefficient of the rotation of the ester in aqueous solution is opposite to that of the pure ester. Further, the dis-

solution of sodium chloride in an aqueous solution of methyl malate not only depresses the lævorotation, but again reverses the temperature-coefficient, that is to say, rise of temperature is now accompanied by an increase in the magnitude of the rotatory power. The rotation in a concentrated solution of barium bromide is positive in sign.

At the outset of this investigation, the hope was expressed that a comparative study of certain compounds of similar constitution would reveal some connexion between the influence of the solvent on the optical rotatory power and the relative configuration of the active compound. When ordinary *d*-tartaric acid is partly reduced with hydriodic acid, it yields *d*-malic acid (Bremer, *Ber.*, 1875, **8**, 1594; Freudenberg, *Ber.*, 1914, **47**, 2037). It is therefore evident that ordinary *l*-malic acid possesses a configuration opposite to that of *d*-tartaric acid. The changes in the rotatory powers of *l*-malic acid and methyl *l*-malate effected by water and by sodium chloride are opposite in character to the corresponding changes undergone by *d*-tartaric acid and by methyl and ethyl *d*-tartrates.* Consequently, the rotatory powers of the configuratively similar compounds, *d*-malic acid (and its esters) and *d*-tartaric acid (and its esters) would show changes of a similar character under the solvent influence of water and sodium chloride respectively. The same regularity is exhibited in the influence of many other solvents on the rotatory powers of methyl malate (Grossmann and Landau) and ethyl tartrate (Patterson, Grossmann, Walden). In this connexion, reference must also be made to the regularity observed by Pickard and Kenyon in the rotatory powers of esters of the optically active β-alcohols in various solvents (T., 1914, **105**, 835). These authors assert that "the action of the four solvents which were most frequently employed had each a specific and (at least in a qualitative, if not also in a quantitative, sense) a common action on the rotatory powers of all the esters."

The conclusion may therefore be drawn that sodium and barium haloids (and probably most inorganic salts) in aqueous solution exert a specific effect on the rotatory power of those hydroxy-derivatives of succinic acid which contain a carboxyl or carbalkyloxy- (ester) group, this effect being usually opposite to that caused by dilution. The author is at present making experiments in order to ascertain whether inorganic salts have a similar effect on the rotatory powers of amino-derivatives of succinic acid.

* For example, the dextrorotation exhibited by *l*-malic acid in concentrated aqueous solution is increased by the dissolution of sodium chloride, whereas the dextrorotation of *d*-tartaric acid in aqueous solution in decreased by the same salt.

Experimental.

The methyl hydrogen tartrate used in these experiments was prepared by Guérin's method (*Annalen*, 1837, **22**, 248). After two crystallisations from ethyl acetate, and a further crystallisation from water, the product was found to contain one molecule of water of crystallisation, and to melt at 75—77°, whereas Walden gives 75—76° (*Ber.*, 1897, **30**, 2891) and Marckwald and Karczag give 76° (*Ber.*, 1909, **42**, 1518).

Methyl Hydrogen Tartrate in Water.

$p = 9{\cdot}68$.

t	15°	25°	40°	55°	63°	25°*
d	1·034	1·030	1·024	1·019	1·016	—
a^t_D ($l=2$)	+3·15°	3·19	3·22	3·23	3·24	—
$[a]^t_D$	+15·7°	16·0	16·3	16·4	16·5	*16·0*

* The values for the specific rotatory powers at 25° recorded in this paper have been obtained by interpolation.

$p = 19{\cdot}67$.

t	14°	24°	31°	40°	50°	25°
d	1·068	1·065	1·062	1·058	1·053	—
a^t_D ($l=2$)	+6·03°	6·15	6·25	6·35	6·44	—
$[a]^t_D$	+14·4°	14·7	15·0	15·3	15·5	*14·8*

Methyl Hydrogen Tartrate in Aqueous Sodium Chloride.

Methyl hydrogen tartrate (2·143 grams) in water (20 grams), $p_1 = 9{\cdot}68$; weight of sodium chloride added, 5·85 grams (0·1 gram-mol. weight), $p = 7{\cdot}65$.

t	16°	20°	28°	42°	48°	25°
d	1·180	1·179	1·178	1·175	1·173	—
a^t_D ($l=2$)	+0·65°	0·73	0·88	1·12	1·22	—
$[a]^t_D$	+3·6°	4·0	4·9	6·2	6·8	*4·6*

Methyl hydrogen tartrate (5·015 grams) in water (20 grams), $p = 20{\cdot}05$; weight of sodium chloride added, 5·85 grams (0·1 gram-mol. weight), $p = 16{\cdot}25$.

t	16°	24°	30°	38°	48°	25°
d	1·208	1·203	1·200	1·195	1·189	—
a^t_D ($l=2$)	+1·04°	1·42	1·69	1·94	2·26	—
$[a]^t_D$	+2·6°	3·6	4·3	5·0	5·9	*3·7*

Methyl Hydrogen Tartrate in Aqueous Barium Bromide.

Methyl hydrogen tartrate (4·86 grams) in water (20 grams), $p = 19{\cdot}6$; weight of barium bromide added, 14·86 grams (0·05 gram-mol. weight), $p = 12{\cdot}24$, d^{25}_4 1·538, a^{25}_D ($l=2$) −3·15°, $[a]$ −8·37°.

Sodium Hydrogen Tartrate in Water.

This salt, which was crystallised twice from water and dried in air, contained one molecule of water of crystallisation.

$p=1{\cdot}961$ (1 gram in 50 grams of water).

$t.$	$d.$	a^t_{ye} $(l=4)$.	$a^t_{gr.}$	$[a]^t_{gr.}$	Hg^{yellow}_{green}.
18°	1·009	+1·80°	+1·98°	+25·0°	0·909
27	1·007	1·84	2·04	25·8	0·902
37	1·003	1·84	2·04	25·9	0·902
43	1·001	1·85	2·04	26·0	0·907
54	0·997	1·84	2·03	26·0	0·906
66	0·991	1·84	2·03	26·1	0·906

$p=13{\cdot}04$ (7·5 grams in 50 grams of water).

23·5°	1·069	+12·78°	+14·25°	+25·6°	0·897
31	1·066	12·90	14·37	25·9	0·898
41	1·063	12·94	14·48	26·1	0·894
48	1·058	12·99	14·49	26·2	0·896
53	1·056	13·00	14·50	26·3	0·897
63	1·053	12·93	14·43	26·3	0·896

$p=4{\cdot}762$ (2·5 grams in 50 grams of water).

$t.$	$d.$	a^t_D $(l=4)$.	$a^t_{ye.}$	$a^t_{gr.}$	$[a]^t_{D.}$	$[a]^t_{gr.}$	$a_D/a_{gr.}$	$a_{ye}/a_{gr.}$
19°	1·024	+4·25°	+4·37°	+4·88°	+21·8°	25·0°	0·871	0·895
25	1·021	4·31	4·46	4·97	22·1	25·5	0·867	0·897
32	1·020	4·35	4·50	5·03	22·4	25·9	0·865	0·895
39	1·018	4·36	4·55	5·05	22·4	26·0	0·863	0·901
44	1·016	4·35	4·53	5·03	22·5	26·0	0·865	0·901
65	1·006	4·30	4·50	5·00	22·5	26·1	0·860	0·900

$p=9{\cdot}091$ (5·0 grams in 50 grams of water).

23°	1·047	+8·34°	+8·68°	+9·68°	+21·9°	+25·4°	0·862	0·897
30	1·043	8·46	8·75	9·75	22·3	25·7	0·868	0·897
39	1·040	8·50	8·80	9·82	22·4	25·9	0·866	0·896
44	1·038	8·51	8·82	9·85	22·5	26·1	0·864	0·896
55	1·032	8·44	8·77	9·76	22·5	26·0	0·865	0·899
66	1·027	8·38	8·72	9·73	22·5	26·1	0·861	0·896

Sodium Hydrogen Tartrate in Aqueous Sodium Chloride.

Sodium hydrogen tartrate (2·5 grams) and sodium chloride (2·925 grams) in water (50 grams).

$p=4{\cdot}51$.

$t.$	$d.$	a^t_D $(l=4)$.	$a^t_{ye.}$	$a^t_{gr.}$	$[a]^t_{D.}$	$[a]^t_{gr.}$	$a_D/a_{gr.}$	$a_{ye}/a_{gr.}$
17°	1·064	+3·76°	+3·89°	+4·35°	+19·6°	+22·7°	0·864	0·894
21	1·062	3·87	4·01	4·47	20·2	23·3	0·866	0·897
36	1·056	3·91	4·04	4·50	20·5	23·6	0·869	0·898
47	1·051	3·93	4·07	4·53	20·7	23·9	0·868	0·898
60	1·044	3·92	4·06	4·52	20·8	24·0	8·867	0·894
68	1·040	3·87	4·01	4·49	20·6	23·9	0·862	0·893

Sodium hydrogen tartrate (1 gram) and sodium chloride in water (50 grams).

p.	Sodium chloride.	Gram-mol. weight.	d_4^{25}.	a_{gr}^{25} ($l=4$).	$[a]_{gr.}^{25}$
1·961	None	—	1·007	—	+25·7°
1·854	2·925	0·05	1·046	+1·79°	23·1
1·76	5·85	0·1	1·085	1·59	20·8
1·60	11·70	0·2	1·144	1·35	18·5

Malic Acid in Water.

$p=16·67$ (10 grams in 50 grams of water).

t	9°	17·5°	28°	32°	41°	45·5°	*25°*
d	1·069	1·066	1·062	1·060	1·057	1·055	—
a_D^t ($l=4$) ...	−0·46°	−0·80	−1·16	−1·30	−1·58	−1·72	—
$[a]_D^t$	−0·65°	−1·13	−1·64	−1·84	−2·24	−2·45	*−1·55*

Malic Acid in Aqueous Sodium Chloride.

Malic acid (10 grams) and sodium chloride (11·7 grams) in water (50 grams).

$p=13·95$.

t	10°	20·5°	32·5°	38·5°	47·5°	62°	*25°*
d	1·162	1·156	1·150	1·147	1·142	1·134	—
a_D^t ($l=4$) ...	+4·06°	+3·36	+2·68	+2·39	+1·92	+1·28	—
$[a]_D^t$	+6·28°	+5·21	+4·17	+3·73	+3·01	+2·02	*+4·80*

Malic Acid in Aqueous Barium Bromide.

Malic acid (10 grams) and barium bromide (29·72 grams) in water (50 grams).

$p=11·15$, d_4^{25} 1·466, a_D^{25} ($l=2$) +7·15°, $[a]_D^{25}$ +21·8°.

Methyl Malate.

The methyl malate used in these experiments was prepared by the Fischer-Speier method (*Ber.*, 1895, **28**, 3254) and fractionated until the rotatory power was constant. The specific rotation was $[a]_D^{20}$ −6·84°; Frankland and Wharton give $[a]_D^{20}$ −6·84° (T., 1899, **75**, 339), and Walden gives $[a]_D^{20}$ −6·85° (*Zeitsch. physikal. Chem.*, 1895, **17**, 248).

t.	d.	a_D^t ($l=1$).	$a_{ye.}^t$	$a_{gr.}^{t\,\prime}$	$[a]_{D.}^t$	$[a]_{gr.}^t$	$a_D/a_{gr.}$	$a_{ye}/a_{gr.}$
15°	1·238	−8·42°	−8·63°	−9·43°	−6·80°	−7·62°	0·893	0·915
50	1·200	8·49	8·71	9·51	7·08	7·93	0·893	0·916
70	1·179	8·44	8·66	9·46	7·16	8·02	0·892	0·915
100	1·149	8·41	8·64	9·43	7·31	8·20	0·892	0·916
25					*6·90*			

Methyl Malate in Water.

$p=9{\cdot}73$.

t	12°	22°	36°	50°	*25°*
d	1·024	1·020	1·014	0·998	—
α_D^t ($l=4$)	−4·41°	4·23	4·01	3·78	—
$[\alpha]_D^t$	−11·07°	10·65	10·16	9·64	*10·51*

$p=50{\cdot}0$.

t	11°	22°	33°	42°	53°	*25°*
d	1·125	1·117	1·109	1·103	1·094	—
α_D^t ($l=2$)	−10·21°	9·66	9·22	8·94	8·50	—
$[\alpha]_D^t$	−9·08°	8·65	8·31	8·12	7·77	*8·58°*

$p=25$, d_4^{25} 1·054, α_D^{25} ($l=2$) −5·07°, $[\alpha]_D^{25}$ −9·62°.

Methyl Malate in Aqueous Sodium Chloride.

Methyl malate (20 grams) in water (20 grams), $p=50$. Sodium chloride added, 5·85 grams.

$p=43{\cdot}6$.

t	12·5°	17·5°	30°	36°	50°	*25°*
d	1·214	1·210	1·201	1·196	1·184	—
α_D^t ($l=2$)	−1·36°	1·49	1·77	1·93	2·31	—
$[\alpha]_D^t$	−1·29°	1·41	1·69	1·85	2·24	*1·65*

Methyl malate (2·222 grams) in water (20 grams), $p=10{\cdot}0$. Sodium chloride added, 5·85 grams.

$p=7{\cdot}91$.

t	11·5°	17°	22·5°	31·5°	42°	53°	*25°*
d	1·182	1·179	1·176	1·171	1·165	1·158	—
α_D^t ($l=4$)...	−0·78°	0·86	0·90	0·95	0·97	1·00	—
α_D^t	−2·1°	2·3	2·4	2·5	2·6	2·7	*2·4°*

Methyl Malate in Aqueous Barium Bromide.

Methyl malate (20 grams) in water (20 grams), $p=50$. Barium bromide added, 14·86 grams.

$p=36{\cdot}4$.

t	11°	19·5°	28·5°	36°	46°	*25°*
d	1·439	1·431	1·423	1·417	1·408	—
α_D^t ($l=1$)	+6·20	5·36	4·76	4·20	3·64	—
$[\alpha]_D$	+11·83	10·30	9·20	8·14	7·10	*9·00*

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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XI.—*Ammonium Perhaloids.*

By Frederick Daniel Chattaway.

Several ammonium trihaloids have been prepared in order to compare them with the diazonium trihaloids, which, erroneously, have been regarded as similarly constituted.

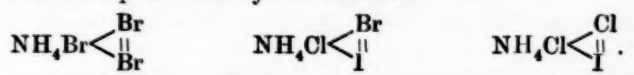
Ammonium tribromide (*Ber.*, 1881, **14**, 2398), ammonium dibromoiodide (*Amer. Chem. J.*, 1900, **24**, 30), and ammonium tri-iodide (T., 1878, **33**, 397) have been described, but apparently no attempts have been made hitherto to obtain the trihaloids containing chlorine.

Two of the latter compounds, namely, *ammonium dichloroiodide*, NH_4Cl_2I, and *ammonium chlorobromoiodide*, NH_4ClBrI, are described in this paper. They are well crystallised and remarkably stable substances which can be kept without change for years, and can even be heated for many hours at 180—200° in sealed tubes without permanent alteration, partial dissociation into ammonium chloride and iodine chloride or bromide only taking place.

When heated in the air or exposed over lime in a vacuum, they lose halogen, ammonium chloride in each case being left. Both are extremely readily soluble in water, and deliquesce in presence of moisture.

A comparison of the properties of the ammonium trihaloids and of the diazonium trihaloids shows that they cannot be regarded as analogously constituted. For example, ammonium perbromide is extraordinarily readily soluble in water, and loses two-thirds of its bromine if exposed for a few minutes in the air, whilst benzenediazonium perbromide is insoluble in water, and can be kept in a vacuum over lime for a long period without any loss of halogen. Similar differences are observed between the other ammonium and diazonium perhaloids. There is, in fact, no resemblance whatever between the two classes of compounds except the unessential one that each contains three atoms of halogen.

The diazonium perhaloids are not perhaloids at all, but *N*-trihalogen derivatives of the hydrazines; for example, benzenediazonium perbromide has the constitution $C_6H_5{\cdot}NBr{\cdot}NBr_2$, whilst the ammonium trihaloids may provisionally be regarded as having a constitution represented by the formulæ



Several trihaloids of aliphatic primary amines have also been prepared; they closely resemble the similarly constituted ammonium trihaloids, but are even more readily soluble in water.

Ammonium Perbromide, NH_4Br_3.

Ammonium perbromide was first obtained by Roozeboom (*Ber.*, 1881, **14**, 2398) by dissolving bromine in a saturated aqueous solution of ammonium bromide, and concentrating over sulphuric acid. He describes it as crystallising in columnar crystals, somewhat resembling potassium dichromate in colour.

Ammonium bromide combines with bromine, not only in aqueous solution, but also in the solid state. If powdered ammonium bromide is placed in a stoppered bottle with the calculated amount of bromine, or exposed, together with liquid bromine, in a closed space, combination slowly takes place, and the white bromide becomes ultimately completely converted into the orange-coloured, crystalline perbromide.

It can also be prepared, although the action is somewhat violent, by adding a concentrated solution of ammonia to excess of liquid bromine cooled in a freezing mixture.

Ammonium perbromide can be preserved unchanged only in the presence of free bromine. Its dissociation pressure at 15° is approximately 0·45 cm., and at 45° approximately 2·5 cm., of mercury.

To ascertain its stability, a quantity which had been kept in a sealed tube for four years was analysed by heating a known amount at 100° and weighing the ammonium bromide left, by titrating the iodine liberated when a weighed amount was added to an excess of a solution of potassium iodide acidified with acetic acid, and by ascertaining the amount of silver bromide precipitated by silver nitrate after reducing a known amount of the salt by sodium sulphite:

1·2138 gave 0·4580 NH_4Br. Br = 62·26.

0·7036 liberated I = 54·5 c.c. *N*/10-iodine. Br = 61·90.

0·4976 gave 1·0859 AgBr. Br = 92·87.

NH_4Br_3 requires $\frac{3}{5}$Br = 62·0. Total Br = 93·02 per cent.

A quantity was heated in a sealed tube for eight hours to 180°; it was then set aside for four years, and again heated to 180—200° for eight hours. On opening the tube, it was found that no nitrogen or hydrogen bromide had been produced, and, except for the formation of a slight superficial layer of ammonium bromide due to dissociation, some little bromine vapour escaping on opening the tube, the compound had apparently undergone no change.

Ammonium Dichloroiodide, NH_4Cl_2I.

This compound was prepared by suspending ammonium chloride in its own weight of water, adding slightly more than an equivalent

amount of powdered iodine, and passing in a rapid stream of chlorine until the free iodine had just disappeared, a point easily recognised by the change of colour. The liquid became distinctly warm during the passage of the chlorine, and on allowing it to remain overnight in a desiccator over sulphuric acid, ammonium dichloroiodide crystallised out in stout, transparent scarlet prisms. These were rapidly collected, pressed between filter paper, and dried over phosphoric oxide, a few crystals of iodine monochloride having been previously placed in the desiccator.

It is equally easily prepared by passing chlorine through a warm, saturated aqueous solution of ammonium iodide. The iodine is first set free, and then disappears, leaving a bright red solution, which deposits ammonium dichloroiodide on cooling.

It was analysed in the manner already described:

0·7122 gave 0·1756 NH_4Cl. ICl = 75·34.
0·7050 liberated I = 65·4 c.c. *N*/10-iodine. ICl = 75·31.
0·4446 gave 1·0698 AgCl + AgI.
NH_4Cl_2I requires ICl = 75·21 per cent. and 1·0739 AgCl + AgI.

Ammonium dichloroiodide is the most stable of the trihaloids. It can be kept for an indefinite period without change if sealed up in a tube, but loses iodine monochloride slowly when exposed to dry air at the ordinary temperature, fairly quickly when exposed in a vacuum over lime, and very quickly when heated in the air to 100°, leaving ammonium chloride.

A specimen kept for four years in a sealed tube was found on analysis not to have altered in composition, and a quantity heated in a sealed tube for eight hours to 180°, kept for four years, and again heated for eight hours to 180—200°, was found to have undergone no change, no nitrogen chloride, nitrogen, or halogen acid being produced.

It is very readily soluble in water, giving a deep red solution.

If through a saturated aqueous solution a stream of chlorine is passed as long as the gas is absorbed, some heat is evolved, and a bright yellow liquid is obtained, which on cooling deposits ammonium tetrachloroiodide, NH_4Cl_4I, in long, golden-yellow prisms. This compound, which was the first of the ammonium perhaloids to be described, having been obtained by Filhol (*J. Pharm.*, 1839, **25**, 431) early in last century, can also be kept without change for an indefinite period if sealed up in a tube.

A specimen kept for four years thus sealed up showed an unaltered composition on analysis. What is more surprising is that it can be heated in a sealed tube for sixteen hours at 180—200° without any production of nitrogen chloride, nitrogen, or halogen

acid. Partial dissociation into chlorine and dichloroiodide no doubt takes place, but these re-combine on cooling.

On exposure to air or in a vacuum over lime, ammonium tetrachloroiodide first loses chlorine, forming the dichloroiodide, which then on further exposure loses iodine monochloride, leaving ammonium chloride.

Ammonium Chlorobromoiodide, NH_4ClBrI.

Ammonium chlorobromoiodide was prepared by dissolving ammonium chloride in its own weight of warm water, and adding an equivalent amount of bromine and of iodine. A deep, brownish-red liquid was thus produced, which on cooling in a desiccator over sulphuric acid deposited the perhaloid in large, deep garnet-red prisms. It was separated, dried, and analysed as described above:

0·5347 gave 0·1092 NH_4Cl. IBr = 79·57.

0·5420 liberated I = 41·5 c.c. $N/10$-iodine. IBr = 79·18.

0·5676 gave 1·2316 AgBr + AgI.

NH_4ClBrI requires IBr = 79·45 per cent. and 1·2388 AgBr + AgI.

Ammonium chlorobromoiodide is a very stable compound, and can be kept in a sealed tube or heated to 200° without decomposition other than temporary partial dissociation into ammonium chloride and iodine bromide.

When heated in air or exposed over lime in a vacuum it loses iodine bromide and leaves ammonium chloride. It is very readily soluble in water, giving a deep red solution.

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XII.—*Synthesis of Pinacones. Part II.*

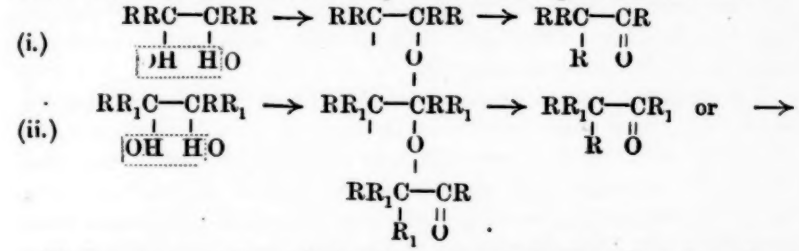
By WILLIAM PARRY.

IN Part I of this research (T., 1911, **99**, 1169) the preparation and properties were described of some unsymmetrical pinacones which were obtained by the interaction of Grignard's reagents and ethyl α-hydroxy*iso*butyrate.

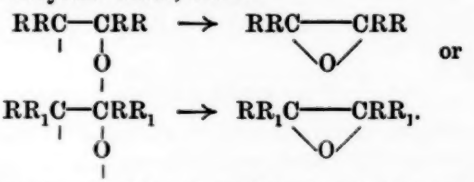
In continuation of this work, the ester has been submitted to the action of magnesium *iso*amyl bromide in dry ethereal solution, and it has been found that *βζ-dimethyl-γ-isoamylheptane-βγ-diol*, $OH{\cdot}CMe_2{\cdot}C(C_5H_{11})_2{\cdot}OH$, is formed in good yield. Reaction also

takes place with magnesium *p*-tolyl bromide, but the pinacone has not been obtained pure.

Now it is well known that symmetrical pinacones of the type $OH{\cdot}CR_2{\cdot}CR_2{\cdot}OH$ or $OH{\cdot}CRR_1{\cdot}CRR_1{\cdot}OH$ lose the elements of water when heated with dilute sulphuric acid, and by the transference of the radicle R or R_1 from the one carbon atom to the other are converted into tertiary ketones or β-pinacolins, thus:



If, however, no "wandering" of the radicle R or R_1 takes place, the free valence of the oxygen atom will attach itself to that of the other carbon atom, and an α-pinacolin will be formed which is a derivative of ethylene oxide, thus:



Benzopinacone is capable of undergoing both transformations, for Thoerner and Zincke (*Ber.*, 1878, **11**, 1396) have shown that the two possible benzopinacolins are produced simultaneously when benzophenone is reduced by zinc and alcoholic hydrogen chloride.

It seemed, then, to be of interest to ascertain if unsymmetrical pinacones of the type $OH{\cdot}CR_2{\cdot}CR'_2{\cdot}OH$ or $OH{\cdot}CR_2{\cdot}CR'R''{\cdot}OH$ reacted in a similar way under the influence of sulphuric acid, and work in this direction was far advanced—and was, indeed, practically completed in respect of β-methyl-γ-ethylpentane-βγ-diol, $OH{\cdot}CMe_2{\cdot}CEt_2{\cdot}OH$, and αα-diphenyl-β-methylpropane-αβ-diol,

$$OH{\cdot}CMe_2{\cdot}CPh_2{\cdot}OH$$

—when Meerwein (*Annalen*, 1913, **396**, 255) published a paper, in the course of which he described these two pinacones and the action of sulphuric acid on them.*

* On communication with Professor Meerwein a division of the work was arranged. After reading Meerwein's paper the author was, for the first time, aware of a dissertation ("Beiträge zur Kenntniss der Pinakone und der Radikalwanderungen bei diesen," Rostock, 1910) by Erdmann, who prepared "*as*-diphenyldimethylpinacone" by the action of magnesium methyl iodide on methyl benzilate, and investigated the action of sulphuric acid on it.

The unsymmetrical pinacones which have so far been investigated are of the type $OH\cdot CMe_2\cdot CR_2\cdot OH$, where R = ethyl, *n*-propyl, *iso*amyl, and phenyl, and it has been found that: (1) they readily undergo the pinacolin rearrangement; (2) when R = alkyl, the pinacolin has the constitution $CMe_2R\cdot COR$, and is identical with that obtained from the corresponding symmetrical pinacone; (3) when R = phenyl, γγ-diphenylbutan-β-one, $CMePh_2\cdot COMe$, is formed, and is the same pinacolin as that prepared by Thoerner and Zincke (*Ber.*, 1878, **11**, 1989) by reduction of acetophenone with alcoholic hydrogen chloride.

The constitution of these tertiary ketones was determined by oxidation, either with chromic acid mixture or with chromic acid in glacial acetic acid. Some difficulty was experienced in the cases where R = *n*-propyl and *iso*amyl. When the former oxidising agent was employed, the alkyl radicle of the group ·COR was alone oxidised; but with the latter agent, the acid $CMe_2R\cdot CO_2H$ was isolated, although the quantity obtained was insufficient for purification for analysis.

Experiments are now being conducted with the pinacones prepared from ethyl α-hydroxy-α-methylbutyrate with the object of gaining further insight into the mechanism of the "pinacolin transformation."

Experimental.

Action of Sulphuric Acid on β-Methyl-γ-ethylpentane-βγ-diol, $OH\cdot CMe_2\cdot CEt_2\cdot OH$: *δδ-Dimethylhexan-γ-one,* $CMe_2Et\cdot COEt$.

This reaction has been studied by Meerwein (*loc. cit.*), who employed ice-cold, concentrated sulphuric acid, and purified the product by way of the semicarbazone.

The pinacolin can also be obtained by heating the pinacone for several hours on the boiling-water bath with an excess of sulphuric acid diluted with its own volume of water. After distillation in a current of steam, the oil is fractionated once under diminished pressure and twice under atmospheric pressure. (Found, C = 74·8; H = 12·45. Calc., C = 75; H = 12·5 per cent.)

Oxidation of the oil to αα-dimethylbutyric acid proved that this pinacolin is identical with that obtained by Lawrinowitsch (*Annalen*, 1877, **185**, 124) by heating the corresponding symmetrical pinacone with dilute sulphuric acid.

Meerwein (*loc. cit.*) carried out the oxidation with sodium hypobromite, and obtained a good yield of αα-dimethylbutyric acid.

* The action of sulphuric acid on *s*-dimethyldi*iso*amylethylene glycol does not appear to have been investigated; but, judging from analogy to the diethyl- and dipropyl-pinacones, it should yield the same pinacolin as the unsymmetrical compound.

In the author's experiments chromic acid mixture was employed, when, in addition to the above-mentioned acid, there were formed: (1) carbon dioxide; (2) acetic acid, which was identified by analysis of the silver salt (Found, Ag = 64·8. Calc., Ag = 64·7 per cent.); and (3) a small quantity of a dark green chromium compound, which was found to be soluble in ether and to separate, on spontaneous evaporation of the solvent, in green crystals. This compound was distilled with 30 per cent. sulphuric acid, and the distillate neutralised with sodium hydroxide, evaporated, and acidified. After extraction with ether and removal of the solvent, a small amount of an oily acid was left, which was converted into the *silver* salt:

0·2103 gave 0·1019 Ag. Ag = 48·4.

$C_6H_{11}O_2Ag$ requires Ag = 48·4 per cent.

It is thus seen that the green substance is a compound of chromic oxide with *αα*-dimethylbutyric acid.

Action of Sulphuric Acid on β-Methyl-γ-propylhexane-βγ-diol, $OH\cdot CMe_2\cdot CPr^{\alpha}_2\cdot OH$: *εε-Dimethyloctan-δ-one,* $CMe_2Pr^{\alpha}\cdot COPr^{\alpha}$.

The pinacone, β-methyl-γ-propylhexane-βγ-diol, has now been obtained in colourless needles arranged in rosettes, which melt at 30°. It was added gradually, in quantities of 25 grams, to concentrated sulphuric acid (100 c.c.) cooled to −5°. After keeping for two hours at the ordinary temperature, the yellowish-red solution was poured on ice (500 grams) and extracted with ether. The ethereal solution was dried, the solvent removed, and the residual oil fractionated under diminished pressure, when the bulk of it distilled at 80—86°/20 mm. (Yield, 36 grams from 50 grams of the pinacone.) This was then distilled in a current of steam, and the yellow oil extracted and fractionated, when it boiled at 182—186°/765 mm.:

0·1350 gave 0·3796 CO_2 and 0·1556 H_2O. C = 76·69; H = 12·8.

$C_{10}H_{20}O$ requires C = 76·85; H = 12·9 per cent.

εε-Dimethyloctan-δ-one is a colourless oil with a faint odour of peppermint. It is obtained as a yellow oil when the pinacone is heated on the boiling-water bath with an excess of 75 per cent. sulphuric acid, and is, in all probability, identical with the pinacolin prepared by Szymanski (*Ber.*, 1886, **19**, 1532) by heating "*s*-dimethyldipropylglycol" with dilute sulphuric acid (20 per cent.). He described it as a yellow oil of camphoraceous odour, boiling at 182—187°, and concluded that it was not a methyl ketone, since it did not combine with sodium hydrogen sulphite.

The *semicarbazone* is formed with difficulty, and in poor yield, when a mixture of the pinacolin (2 grams), semicarbazide hydro-

chloride (2 grams), and fused sodium acetate (2·5 grams) in aqueous alcoholic solution is heated on the water-bath for two hours and kept for several days, with frequent shaking. It separates from dilute alcohol, in which it is readily soluble, in white needles, which melt at 145°:

0·1353 gave 0·3068 CO_2 and 0·1374 H_2O. C = 61·84; H = 11·28.

$C_{11}H_{23}ON_3$ requires C = 61·91; H = 10·88 per cent.

The constitution of the pinacolin was proved by oxidation (1) with chromic acid mixture, (2) with chromic acid in glacial acetic acid.

The oil (5 grams) was heated on the boiling-water bath with potassium dichromate (15 grams) dissolved in 250 c.c. of dilute sulphuric acid (15 per cent.), when carbon dioxide was evolved in quantity. After four days' heating water was added, and the liquid distilled until the distillate had no longer an acid reaction. On filtering the contents of the flask, a very small amount of a green chromium salt was obtained. The distillate was neutralised with sodium hydroxide and evaporated to dryness on the water-bath, when about 10 grams of sodium salt were left (from 15 grams of ketone).

On decomposition of the sodium salt with sulphuric acid, an acid separated, which was extracted with ether, the solvent removed after drying, and the oil fractionated. Two fractions were collected, (*A*) from 100° to 130°, and (*B*) from 135° to 145°. The latter, which formed the bulk of the product, was analysed:

0·1688 gave 0·2943 CO_2 and 0·1211 H_2O. C = 47·55; H = 7·9.

0·3531 Ag salt gave 0·2102 Ag. Ag = 59·5.

$C_3H_6O_2$ requires C = 48·65; H = 8·1 per cent.

$C_3H_5O_2Ag$ requires Ag = 59·6 per cent.

The oil (*B*) was evidently propionic acid contaminated with a very little acetic acid.

The only evidence of the formation of *αα*-dimethylvaleric acid was the presence of the above-mentioned green chromium compound, which weighed less than half a gram.

The pinacolin (6 grams) was next dissolved in glacial acetic acid (50 c.c.), heated to 70° on a water-bath, and a solution of chromium trioxide (6 grams) in glacial acetic acid (60 c.c.) slowly run in from a dropping-funnel. After heating for a day, water was added, the solution extracted with ether, the extracts well washed, and dried over anhydrous magnesium sulphate. The ether was distilled, and the product neutralised with sodium hydroxide, when a quantity of unoxidised oil remained, which was removed by means of ether. The alkaline solution was evaporated, acidified, extracted, and the ether expelled. The residual oil was heated on

the boiling-water bath for several hours under 50 mm. pressure to remove acetic acid, when about 1 gram was left, which was insufficient for purification by distillation. It was converted into the *silver* salt:

0·3729 gave 0·1724 Ag. Ag = 46·2.

$C_7H_{13}O_2Ag$ requires Ag = 46 per cent.

It thus appears that αα-dimethylvaleric acid is formed by the oxidation of this pinacolin, which, therefore, has the constitution $CMe_2Pr^{\alpha}\cdot COPr^{\alpha}$.

*βζ-Dimethyl-γ-iso**amyl**heptane-βγ-diol*, $OH\cdot CMe_2\cdot C(C_5H_{11})_2\cdot OH$.

For the preparation of this pinacone, magnesium turnings (24 grams) were covered with dry ether (300 c.c.), and a little *iso*amyl bromide was added. The flask was warmed on the water-bath until reaction commenced, when a solution of *iso*amyl bromide (150 grams) and ethyl α-hydroxy*iso*butyrate (33 grams) in dry ether (100 c.c.) was dropped in at such a rate that the mixture boiled gently (Davies and Kipping, T., 1911, **99**, 296). When all had been added, the flask was heated for two hours, and left overnight.

After decomposition with ice and dilute sulphuric acid, and the separation of the ethereal solution, the aqueous liquid was extracted twice, the combined extracts washed with water and dilute sodium sulphite solution, and dried over anhydrous magnesium sulphate. The ether was then removed, and the yellow oil which was left was twice fractionated under diminished pressure, when a colourless liquid passed over, and solidified in the receiver to a white solid resembling wax. After a day's contact with porous porcelain, which absorbed a little adhering oil, the yield of pure material was 30 grams (52 per cent. of the theoretical):

0·1782 gave 0·4733 CO_2 and 0·2132 H_2O. C = 72·44; H = 13·29.

0·354 in 18·53 benzene gave $\Delta t = -0·388$. M.W. = 246.

0·797 „ 18·53 „ „ $\Delta t = -0·781$. M.W. = 275.

$C_{14}H_{30}O_2$ requires C = 72·9; H = 13·1 per cent. M.W. = 230.

*βζ-Dimethyl-γ-iso**amyl**heptane-βγ-diol* boils at 150°/20 mm., and solidifies, on cooling, in clusters of white, waxy needles, radiating from a point. It melts at 34—35°, and is very readily soluble in all the common organic media. It has the distinctive odour characteristic of *iso*amyl compounds. Its symmetrical isomeride has already been prepared by Rohn (*Annalen*, 1878, **190**, 311) by reduction of methyl *iso*amyl ketone, and melts at 30°.

Action of Sulphuric Acid on $\beta\zeta$*-Dimethyl-*γ*-isoamylheptane-*$\beta\gamma$*-diol*, $OH\cdot CMe_2\cdot C(C_5H_{11})_2\cdot OH$: $\beta\zeta\zeta_1$*-Tetramethyldecan-*ϵ*-one*, $C_5H_{11}\cdot CMe_2\cdot CO\cdot C_5H_{11}$.

The pinacone (25 grams) was added gradually to concentrated sulphuric acid (100 c.c.) cooled to $-5°$, the flask being shaken vigorously at intervals. It dissolved slowly, with evolution of heat, and the yellowish-red solution was left for one hour at the ordinary temperature. It was then poured on powdered ice, and distilled in a current of steam.

The distillate was extracted with ether, the solution dried over anhydrous magnesium sulphate, and fractionated, when a quantity (15 grams) boiled at 239—244°/771 mm. On keeping for a few days, the oil became rather dark coloured, from which it appeared that some decomposition had taken place during the distillation under atmospheric pressure. It was therefore fractionated twice under diminished pressure and analysed:

0·1696 gave 0·4888 CO_2 and 0·2048 H_2O. C=78·6; H=13·42.

$C_{14}H_{28}O$ requires C=79·16; H=13·3 per cent.

$\beta\zeta\zeta_1$*-Tetramethyldecan-*ϵ*-one* is a yellow oil, which has not been obtained colourless. It boils at 132—134°/25 mm., and has no odour. Attempts to prepare a semicarbazone were unsuccessful, and this fact indicates that the pinacolin is not a methyl ketone. When it was oxidised with chromic acid mixture, no solid chromium compound was formed, but carbon dioxide was evolved, and, after treatment as previously described, a small amount of an oily acid was obtained, which boiled at 190—195° under atmospheric pressure.

Analysis of the silver salt of this acid (Found, Ag=51·7; $C_5H_9O_2Ag$ requires Ag=51·7 per cent.) proved that *iso*valeric acid had been formed by oxidation of the terminal $\cdot C_5H_{11}$ group.

When, however, the pinacolin was oxidised by chromic acid in glacial acetic acid, an oil was eventually obtained which did not distil from a boiling-water bath when the pressure was diminished to 50 mm. It was pale yellow, very viscid, and had an odour resembling that of *iso*valeric acid. It was insufficient in quantity for further purification, and on analysis gave numbers which indicated that it was still contaminated with acetic acid. (Found, C=63·4, 63·7; H=9·24, 9·03. $C_9H_{18}O_2$ requires C=68·3; H=11·4 per cent.)

It was converted into the *silver* salt:

0·1947 gave 0·0818 Ag. Ag=41·1.

$C_9H_{17}O_2Ag$ requires Ag=40·8 per cent.

The formation of $\alpha\alpha\delta$-trimethylhexoic acid proves that the constitution of the pinacolin is $C_5H_{11}\cdot CMe_2\cdot CO\cdot C_5H_{11}$.

Action of Sulphuric Acid on αα-Diphenyl-β-methylpropane-αβ-diol, $OH\cdot CMe_2\cdot CPh_2\cdot OH$: *γγ-Diphenylbutan-β-one*, $CMePh_2\cdot COMe$.

Erdmann (*loc. cit.*) and Meerwein (*loc. cit.*) effected this transformation by the aid of cold, concentrated sulphuric acid.

In the author's experiments, the pinacone was heated for several hours on the boiling-water bath with excess of sulphuric acid diluted with its own volume of water, and the contents of the flask were then distilled in a current of steam. The product was a pale yellow oil, boiling constantly at 180°/18 mm. (Found, C = 85·8; H = 7·2. Calc., C = 85·66; H = 7·2 per cent.) It solidified when seeded with a crystal of "acetophenone pinacolin," prepared by Thoerner and Zincke's method (*loc. cit.*), and, after pressure on porous porcelain and crystallisation from dilute alcohol, formed snow-white needles, melting at 41°. The semicarbazone was readily formed from the yellow oil (4·7 grams from 5 grams of oil), and crystallised from alcohol in white needles, melting at 175° (Erdmann gives 179°).

Oxidation by chromic acid mixture yielded the αα-diphenylpropionic acid described by Thoerner and Zincke (*Ber.*, 1878, **11**, 1993), thus confirming the identity of the two pinacolins.

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant in aid of the expense of this investigation.

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XIII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XII. The Rotatory Powers of Some Esters of Benzoic and of 1- and 2-Naphthoic Acids with Optically Active Secondary Alcohols.*

By JOSEPH KENYON and ROBERT HOWSON PICKARD.

GENERALLY speaking, the rotatory powers exhibited by the benzoates of dextrorotatory β-butanol, β-hexanol, β-octanol, β-undecanol, γ-nonanol, and benzylmethylcarbinol, both in the homogeneous state and in solvents, are analogous to those of the numerous esters of these carbinols with normal fatty acids, which

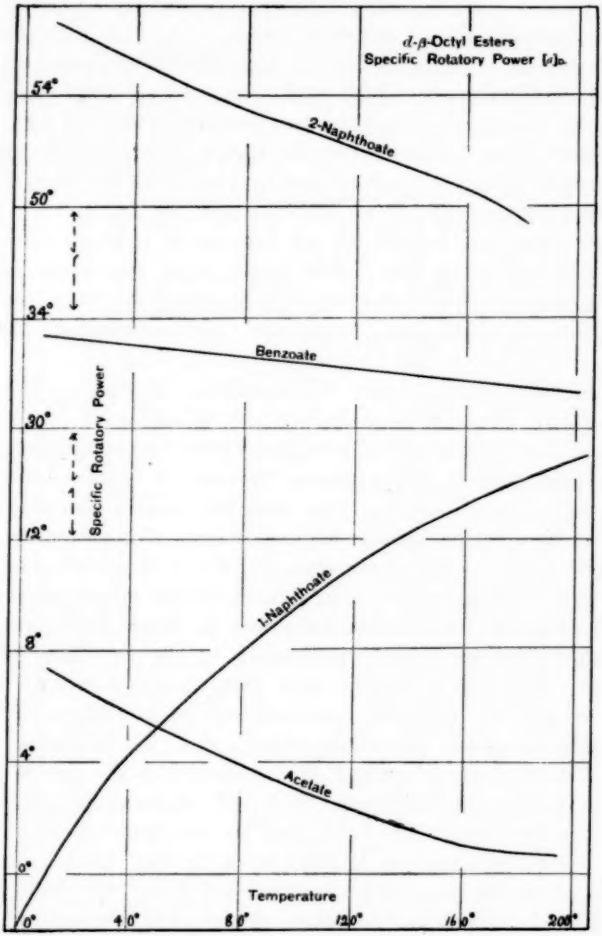
have been described in Parts V, VII, and VIII (T., 1914, **105**, 830, 2226, 2262). Thus in the homogeneous state the curves showing the rotatory powers at different temperatures are linear up to temperatures, in some cases, as high as 100°, after which the temperature-coefficients rapidly alter (usually decrease). As a rule, the optical dispersive power of these esters is simple at the lower temperatures, whilst at the higher temperatures the rotations do not conform to the law of simple dispersive power as expressed by the Drude equation with one term, $\alpha = k/(\lambda^2 - \lambda_0^2)$. Further, the rotatory powers of these esters as exhibited in the homogeneous state at about 20° are altered only to a slight extent by solution in ethyl alcohol, but usually are much depressed by solution in carbon disulphide, whilst it may be stated that, in a qualitative sense, any one solvent has the same effect on the rotations of all the esters. It has been found that in only a few details (mainly connected with solutions) do any of the benzoates differ in their optical properties (as summarised above) from the esters of the fatty acids. These slight and unimportant differences may be ascribed to the influence of the aromatic radicle, which in all cases causes a considerable exaltation of rotatory power, but they serve to emphasise, further, the abnormal behaviour of the esters of 1- and 2-naphthoic acids.

The 1- and 2-naphthoic esters of these same optically active carbinols behave, as regards their rotatory powers, in quite a different manner. Thus the rotatory powers of the 1-naphthoic esters (unlike those of the aliphatic and benzoic esters) usually have large and varying positive temperature-coefficients (at least up to about 150°), whilst all the naphthoic esters have complex dispersive powers at both low and high temperatures. In the case of the 1-naphthoic esters of the carbinols, $CH_3 \cdot CH(OH) \cdot R$, which exhibit in many cases the so-called anomalous dispersion for mercury-violet to sodium-yellow light between temperatures of $-10°$ and $+30°$, the dispersive power has a tendency to become simple at temperatures between 90° and 120°, when the rotations seem to agree with the Drude equation with one term; above 120°, however, the dispersive power is undoubtedly complex, as it is in the case of the 2-naphthoic esters, probably at all temperatures. In Fig. 1 the influence of temperature on the specific rotatory power, $[\alpha]^t_D$, of the *d*-β-octyl esters can be compared. The determinations of the rotatory powers of the naphthoic esters in various solvents give results which are not comparable with those obtained for the rotatory powers of the esters of benzoic and aliphatic acids.

The hypothesis which has been put forward (*loc. cit.*, Parts VI and IX, T., 1914, **105**, 1117, 2647) to explain the complex dis-

persive power of the alkyl-1-naphthylcarbinols and of the esters of aliphatic acids with secondary alcohols (Part V, *loc. cit.*) can be applied consistently to the new compounds described in this com-

FIG. 1.



munication. Thus the complex dispersive power exhibited under some conditions* by almost all the optically active esters hitherto described by us† is assumed to be due to the existence under those

* Notably at the higher temperatures of the experiments.

† Even *d*-β-butyl acetate, which possesses the simplest chemical constitution of any of these esters, has apparently a complex dispersive power in the neighbourhood of its boiling point.

conditions of two isodynamic modifications of the esterified carboxylic group, whilst the complex dispersive power at lower temperatures of the alkyl-1-naphthylcarbinols and the esters of the naphthoic acids is similarly ascribed to the presence, then, in these compounds of two isodynamic modifications of the naphthyl radicle. For each pair of modifications it appears necessary to assume that the two isomerides are of opposite optical sign and have different dispersive powers. Thus, as in the case of the aliphatic esters of alkyl-1-naphthylcarbinols (Part IX, *loc. cit.*), these naphthoic esters can be assumed to contain two dissimilar centres of possible dynamic isomerism of the type postulated (compare in this connexion the like phenomena exhibited by the menthyl esters of some substituted benzoic acids, Part XI, this vol., p. 35).

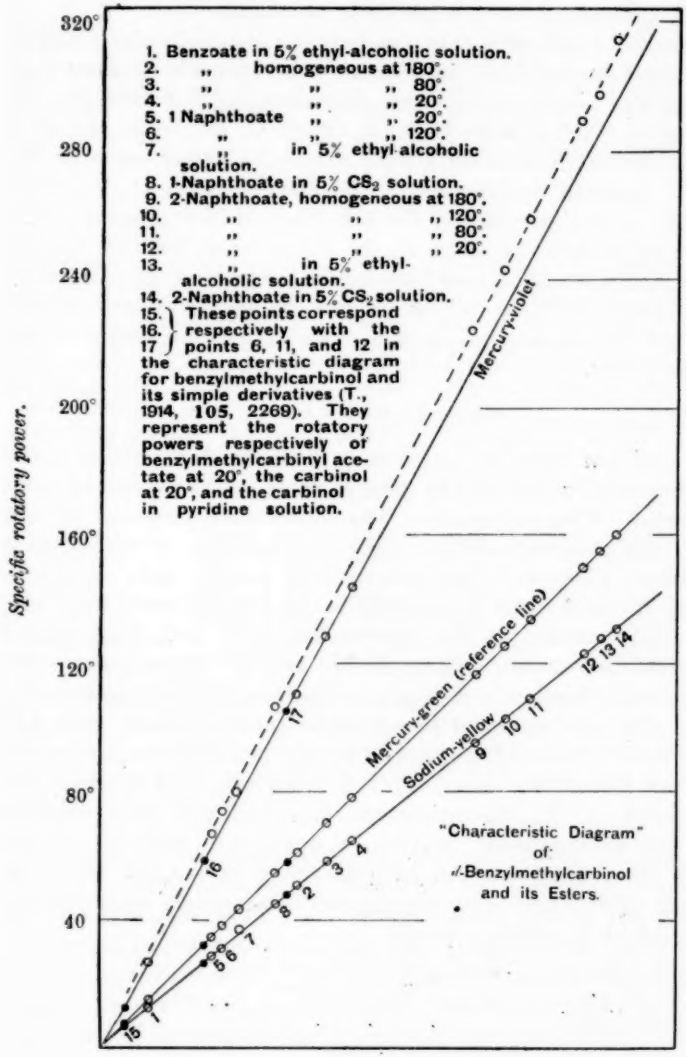
However, whatever hypothesis be adopted to explain the experimental facts, there is now little doubt that the presence of a naphthyl group or of an esterified carboxylic group in an optically active compound is commonly associated with a complex dispersive power.

The theoretical basis of the characteristic diagram, a device of Armstrong and Walker, to correlate the rotations of a compound exhibiting the phenomenon of so-called anomalous dispersion under varying conditions, is the presence in such a compound of two isomerides of opposite optical sign and different dispersive power, each of which retains under all conditions a constant rotatory power. The success with which such a method of plotting rotations has been extended (admittedly in a more or less empirical manner) to groups of allied compounds described in these investigations is emphasised by its successful application to the rotations of these new esters. Thus it is found that the rotatory powers of the benzoate of any one of these carbinols can be co-ordinated on the characteristic diagram for the carbinol and its aliphatic esters, but that the rotatory powers of the naphthoates do not fit on the diagram. It appears, however, that the rotatory powers of the esters of the two naphthoic acids can be co-ordinated on a second diagram. This phenomenon is illustrated by Fig. 2, the characteristic lines of which have been reproduced from the diagram for *d*-benzylmethylcarbinol and its esters (Part VIII, *loc. cit.*, p. 2269). The values of the rotatory powers of the benzoate and the two naphthoates are here plotted, but only those of the benzoates fall on the original lines, whilst those for the naphthoates appear to fall on the broken line.

It would appear to be a corollary of the hypothesis adopted to explain the complex dispersive power of these substances that rotations, in general, are often the algebraic sum of two or more

magnitudes. In the cases of well-marked complex dispersion, these magnitudes will be positive and negative, whilst each different magnitude will probably coincide with a term in the Drude equa-

FIG. 2.


320°
280
240
200°
160°
120°
80°
40
Specific rotatory power.
1. Benzoate in 5% ethyl-alcoholic solution.
2. ,, homogeneous at 180°.
3. ,, ,, ,, 80°.
4. ,, ,, ,, 20°.
5. 1 Naphthoate ,, ,, 20°.
6. ,, ,, ,, 120°.
7. ,, in 5% ethyl-alcoholic solution.
8. 1-Naphthoate in 5% CS_2 solution.
9. 2-Naphthoate, homogeneous at 180°.
10. ,, ,, ,, 120°.
11. ,, ,, ,, 80°.
12. ,, ,, ,, 20°.
13. ,, in 5% ethyl-alcoholic solution.
14. 2-Naphthoate in 5% CS_2 solution.
15. } These points correspond
16. } respectively with the
17 } points 6, 11, and 12 in the characteristic diagram for benzylmethylcarbinol and its simple derivatives (T., 1914, 105, 2269). They represent the rotatory powers respectively of benzylmethylcarbinyl acetate at 20°, the carbinol at 20°, and the carbinol in pyridine solution.
Mercury-violet
Mercury-green (reference line)
Sodium-yellow
"Characteristic Diagram" of dl-Benzylmethylcarbinol and its Esters.

tion. Some substances known to form isomerides, as, for example, lævulose, appear, however, to be of simple dispersive power when tested by the easy, but somewhat crude, method of plotting the

reciprocals of the rotations against the squares of the wave-lengths. It is probable that the rotatory powers of dynamic isomerides, and the positions of their absorption bands in the remote ultra-violet, are widely different only in a few cases, thus rendering it often very difficult to detect slight departures from the law of simple dispersion with the present methods of polarimetry.

That similar qualitative relations between the molecular rotatory powers should be exhibited in a series of compounds showing complex dispersive power under some conditions, as, for example, the β-octyl esters, $C_6H_{13}\cdot CHMe\cdot O\cdot CO\cdot R$ (Part V, *loc. cit.*), and in a series of compounds showing simple dispersive power, such as the "methyl" series of carbinols, $CH_3\cdot CH(OH)\cdot R$ (Part II, T., 1912, **101**, 626), is not surprising, for the mass of the growing chain would probably have an effect on the rotations of both of the isodynamic modifications of the esters (and none on their dispersive power), similar to that which it has on the rotations of the members of an homologous series of compounds all showing simple dispersive power.

Experimental.

In general, the experimental details of the work described in the present communication are the same as those in the preceding parts of this series of investigations. The esters were prepared by the action of the required acid chlorides on a solution of the carbinol in pyridine. They were not obtained in a solid state except in the cases of the 1- and 2-naphthoates of *d*-benzylmethylcarbinol, which readily remain in the supercooled state, and when seeded set to crystalline masses, melting at 58° and 32° respectively. The benzoates are colourless and highly refractive, but the naphthoates (like the aliphatic esters of the alkyl-1-naphthyl esters, Part IX, *loc. cit.*) have a yellowish tinge, and appear to exhibit a pale yellow and amber dichroism. The carbinols were prepared specially for the purposes of this investigation, and had the same rotatory powers as the specimens previously described. Samples of the carbinols recovered from the esterification process, and also from the esters after these had undergone polarimetric examination, were unaltered in rotatory power.

TABLE I.

Benzoic Esters.

Of	B. p.	D_4^{20}.	n_4^{20}.	$M.(n-1)/d$.	$[M]_{Hg\ violet.}^{20°}$	$[M]_{Hg\ violet.}^{100°}$
d-β-Butanol	120°/20 mm.	1·0018	1·4930	87·6	+139·1°	+118·7°
d-β-Hexanol	144°/19 „	0·9760	1·4897	103·4	+148·8	+142·9
d-β-Octanol	171°/20 „	0·9613	1·4887	118·9	+160·0	+157·7
d-β-Undecanol ...	159°/3·5 „	0·9530	1·4899	141·6	+157·3	+156·6
d-γ-Nonanol	178°/18 „	0·9589	1·4898	126·7	+39·6	+55·4
d-Benzylmethyl-carbinol	197°/18 „	1·0960	1·5560	121·7	+346·9	+300·2

1-Naphthoic Esters.

d-β-Butanol	154°/5 mm.	1·0731	1·5721	121·5	+136·9°	+119·2°
d-β-Hexanol	175°/4 „	1·0436	1·5584	137·0	+ 20·5	+ 61·3
d-β-Heptanol ...	175°/3 „	1·0297	1·5524	144·8	+ 13·1	+ 62·4
d-β-Octanol	175°/2·5 „	1·0185	1·5476	152·7	− 1·1	+ 55·9
d-β-Decanol	195°/2·5 „	1·0040	1·5405	168·2	− 0·1	+ 59·0
d-β-Undecanol ...	205°/2·5 „	0·9917	1·5360	176·1	+ 1·5	+ 59·2
d-γ-Nonanol	187°/3 „	1·0112	1·5442	160·4	−153·1	− 65·2
d-Benzylmethyl-carbinol	204°/3 „	1·1170	1·6041	156·9	+199·1	+212·8

2-Naphthoic Esters.

d-β-Butanol	158°/5 mm.	1·0654	1·5731	122·7	+250·4°	+192·6°
d-β-Hexanol	168°/3 „	1·0400	1·5608	138·0	+326·3	+284·8
d-β-Octanol	176°/3 „	1·0138	1·5500	154·1	+357·4	+332·0
d-β-Undecanol ...	206°/2·5 „	0·9904	1·5376	177·0	+366·0	+348·1
d-γ-Nonanol	190°/3 „	1·0052	1·5454	161·7	+132·7	+162·8
d-Benzylmethyl-carbinol	204°/3 „	1·1121	—	—	+841·5	+728·5

The corresponding values of the molecular rotatory powers exhibited in various solvents are given on p. 129, whilst the values exhibited by the esters in the homogeneous state at various temperatures can be calculated from the values of the specific rotatory powers (see p. 122) which have been deduced from the data there given.

In table II the results of the determinations of the density (D_4^t) and of the rotatory power ($\alpha^{100\ mm.}$) of the esters in the homogeneous state are given, the second set of figures for each ester being the calculated values at the temperatures named of the specific rotatory power. The line of wave-length 4358 (occasionally called mercury *blue*) is designated "mercury violet" throughout this series of investigations.

Table II.

d-β-*Butyl Benzoate*, $CHMeEt{\cdot}O{\cdot}CO{\cdot}C_6H_5$.

Temp.	19·5°	54·5°	90·5°	128°		
D'_4 ...	0·9997	0·9706	0·9368	0·9013		
Temp.	21·5°	43°	70°	121°	155°	176°
α_D.....	+39·10	+36·70	+33·10	+29·12	+26·88	+25·38
Temp.	21·5°	42°	70°	121°	152°	178°
α_{ye} ...	+40·92	38·50	34·42	30·30	28·12	26·32
α_{gr} ...	+46·48	43·66	39·06	34·54	31·96	29·90
Temp.	21·5°	42°	70°	121°	151°	
α_{vi} ...	+78·06	73·60	65·84	58·26	54·38	

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]_D$ ...+	39·23	37·62	36·26	34·86	33·52	32·22	31·20	30·25	29·61
$[\alpha]_{ye}$...	41·06	39·39	37·78	36·24	34·86	33·55	32·41	31·43	30·67
$[\alpha]_{gr}$ ...	46·59	44·64	42·83	41·15	39·45	38·05	36·03	35·88	34·88
$[\alpha]_{vi}$ ...	78·13	75·24	72·34	69·37	66·70	64·29	62·40	61·16	

d-β-*Hexyl Benzoate*, $C_4H_9{\cdot}CHMe{\cdot}O{\cdot}CO{\cdot}C_6H_5$.

Temp.	18·5°	53°	94°	128°	
D'_4.....	0·9773	0·9488	0·9129	0·8831	
Temp.	19°	52°	106·5°	132°	172°
α_D	+34·00	32·86	30·18	29·10	26·06
Temp.	19°	51°	100°	132°	172°
α_{ye}	+36·16	34·50	31·80	30·40	28·40
Temp.	19°	51°	101°	132°	172°
α_{gr}	+41·24	39·28	36·22	34·66	32·44
Temp.	19°	50°	103°	131°	172°
α_{vi}	+70·56	67·66	62·64	60·28	56·40

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$ ...	+35·38	34·93	34·52	34·09	33·62	33·17	32·73	32·21	31·75
$[\alpha]^t_{ye}$ ...	36·99	36·55	36·09	35·60	35·07	34·61	34·32	33·87	33·40
$[\alpha]^t_{gr}$ ...	42·20	41·69	41·15	40·58	40·01	39·56	39·10	38·58	38·14
$[\alpha]^t_{vi}$ ...	72·23	71·52	70·82	70·13	69·36	68·66	67·94	67·19	66·31

d-β-*Octyl Benzoate*, $C_6H_{13}{\cdot}CHMe{\cdot}O{\cdot}CO{\cdot}C_6H_5$.

Temp.	19°	59°	94°	133°		
D'_4 ...	0·9606	0·9298	0·9000	0·8683		
Temp.	20·5°	61°	82°	110°	140°	180°
α_D.....	+31·90	30·42	29·64	28·76	27·68	26·18
Temp.	20·5°	57°	85°	108°	142°	180°
α_{ye} ...	+33·28	31·98	30·90	30·02	28·94	27·60
α_{gr} ...	+38·06	36·52	35·24	34·22	33·00	31·60
Temp.	20·5°	56°	85°	110°	142°	180°
α_{vi} ...	+65·54	63·44	61·28	59·40	57·48	55·16

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$ ...	+33·27	33·11	32·87	32·68	32·47	32·23	32·00	31·78	31·44
$[\alpha]^t_{ye}$...	34·70	34·45	34·32	34·15	33·97	33·79	33·60	33·30	33·20
$[\alpha]^t_{gr}$...	39·65	39·41	39·15	38·87	38·63	38·48	38·29	38·14	37·96
$[\alpha]^t_{vi}$...	68·26	68·17	67·90	67·66	67·39	67·08	66·79	66·48	66·18

d-β-*Undecyl Benzoate*, $C_9H_{19}\cdot CHMe\cdot O\cdot CO\cdot C_6H_5$.

Temp.	18·5°	56°	91°	136·5°				
D^t_4	0·9531	0·9248	0·8985	0·8612				
Temp.	18°	37°	68°	78°	123°	154°	164°	182·5°
α_D	+26·32	25·82	25·04	24·68	23·44	22·52	22·18	21·60
Temp.	18°	35°	62°	86°	122°	151°	168°	178°
α_{ye}.....	+27·58	27·12	26·30	25·60	24·54	23·58	23·04	22·80
Temp.	18°	36°	62°	88°	122°	151°	178°	
α_{gr}.....	+31·42	30·92	30·00	29·12	28·04	27·04	26·00	
Temp.	18°	35°	62°	84°	124°	151°	171°	181°
α_{vi}	+54·42	53·54	52·38	51·30	49·06	47·46	46·22	45·50

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$ ...	+27·55	27·45	27·33	27·18	27·10	26·94	26·72	26·49	26·25
$[\alpha]^t_{ye}$ ...	28·89	28·75	28·61	28·42	28·30	28·12	27·90	27·79	27·46
$[\alpha]^t_{gr}$ ...	32·92	32·77	32·61	32·41	32·28	32·11	32·03	31·66	31·37
$[\alpha]^t_{vi}$ ...	56·99	56·94	56·90	56·79	56·72	56·40	55·01	55·64	55·14

d-γ-*Nonyl Benzoate*, $C_6H_{13}\cdot CHEt\cdot O\cdot CO\cdot C_6H_5$.

Temp.	18°	57°	97·5°	134°				
D^t_4 ...	0·9603	0·9304	0·8986	0·8670				
Temp.	20°	50°	80°	115°	144°	168°	184°	
α_D.....	+6·52	7·80	8·76	9·22	9·58	9·86	9·96	
Temp.	20°	47°	92°	118	144°	168°	184°	
α_{ye} ...	+6·96	8·08	9·22	9·80	10·12	10·44	10·54	
Temp.	20°	48°	92°	118°	144°	168°	184°	
α_{gr} ...	+8·04	9·38	10·68	11·32	11·64	11·90	12·04	
Temp.	20°	47°	92°	121°	144°	168°		
α_{vi} ...	+15·30	17·36	19·62	20·88	21·30	21·72		

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$ ...	+6·84	7·88	8·70	9·33	10·00	10·59	11·10	11·60	12·03
$[\alpha]^t_{ye}$...	7·27	8·21	9·16	9·86	10·52	11·18	11·84	12·24	12·74
$[\alpha]^t_{gr}$...	8·39	9·59	10·57	11·39	12·02	12·88	13·48	13·92	14·50
$[\alpha]^t_{vi}$...	15·95	17·92	19·55	21·07	22·34	23·68	24·75	25·60	26·37

d-*Benzylmethylcarbinyl Benzoate*, $CH_2Ph\cdot CHMe\cdot O\cdot CO\cdot C_6H_5$.

Temp.	17·5°	57°	95°	137°				
D^t_4	1·0975	1·0663	1·0331	0·9985				
Temp.	21°	39°	47°	83°	120°	150°	175°	191°
α_D	+71·12	67·84	66·58	60·48	55·28	52·00	49·60	48·00
Temp.	21°	38°	51°	75°	121°	150°	175°	
α_{ye}.....	+74·50	71·20	68·98	65·00	57·74	54·60	51·76	
Temp.	21°	37°	52°	75	121°	150°	175°	191°
α_{gr}.....	+85·80	82·32	79·34	74·90	66·68	63·96	59·74	57·80
Temp.	21°	37°	50°	82°	121°	150°	175°	
α_{vi}	+158·00	151·84	146·98	134·04	123·10	115·70	111·60	

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$ ...	+65·07	62·73	60·46	58·32	56·41	54·64	53·23	52·08	51·00
$[\alpha]^t_{ye}$ ...	68·14	65·68	63·45	61·38	59·36	57·41	55·77	54·47	53·29
$[\alpha]^t_{gr}$ ...	78·84	75·77	73·24	70·72	68·24	66·20	64·46	62·91	61·45
$[\alpha]^t_{vi}$	144·54	139·75	134·82	129·06	125·10	121·70	118·72	116·25	115·25

d-β-*Butyl* 1-*Naphthoate*, $CHMeEt{\cdot}O{\cdot}CO{\cdot}C_{10}H_7$.

Temp.	18·5°	64°	93°	136°
D^t_4	1·0734	1·0378	1·0144	0·9798

Temp.	8°	22·5°	46°	84°	120°	142°	162°	193°
a_D	+31·40	30·00	28·48	25·74	23·48	22·34	21·56	19·86

Temp.	6°	22·5°	48°	78°	119°	143°	162°	193°
a_{ye}....	+33·20	31·80	29·68	27·36	24·92	23·44	22·62	20·92
a_{gr}.....	+37·80	36·38	33·92	31·20	28·46	26·72	25·56	24·00

Temp.	6°	22·5	47°	76°	119°	143°	161°	192°
a_{vi}	+66	64	60·20	55·50	50·74	48·06	46·50	43·40

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+28·40	27·44	26·42	25·38	24·48	23·65	22·97	22·42	21·90
$[a]^t_{ye}$ ...	29·82	28·76	27·68	26·69	25·72	24·95	24·16	23·46	22·98
$[a]^t_{gr}$ ...	34·00	32·80	31·59	30·47	29·42	28·40	27·48	26·68	26·01
$[a]^t_{vi}$ ...	60·03	57·98	55·85	53·97	52·29	50·85	49·56	48·44	47·35

d-β-*Hexyl* 1-*Naphthoate*, $C_4H_9{\cdot}CHMe{\cdot}O{\cdot}CO{\cdot}C_{10}H_7$.

Temp.	19°	56°	92°	135°
D^t_4	1·0439	1·0174	0·9875	0·9537

Temp.	6°	10°	20°	55°	96°	135°	149°	169°	193°
a_D	+4·72	5·10	6·16	8·86	11·16	12·46	12·94	13·44	13·88

Temp.	4°	8°	20°	55°	95°	135°	149°	171°	193°
a_{ye}.....	+4·34	4·98	6·34	9·14	11·72	13·16	13·64	14·10	14·68
a_{gr}.....	+4·06	5·10	6·84	10·16	13·26	14·98	15·50	16·14	16·66

Temp.	8°	20°	55°	92°	135°	149°	173°	193°	
a_{vi}.....	+5·20	8·34	16·10	22·66	26·56	27·78	29·30	30·40	

Temp.	0°	10°	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+3·96	4·84	5·87	7·48	9·02	10·32	11·54	12·53	13·37	14·14	14·84
$[a]^t_{ye}$ ...	3·53	4·85	6·08	7·82	9·40	10·85	12·14	13·23	14·10	14·88	15·22
$[a]^t_{gr}$ ...	2·97	5·13	6·55	8·55	10·48	12·37	13·82	15·10	16·03	16·98	17·81
$[a]^t_{vi}$ ...	2·95	5·49	8·00	12·53	16·90	20·86	23·95	26·40	28·53	30·53	32·32

d-β-*Heptyl* 1-*Naphthoate*, $C_5H_{11}{\cdot}CHMe{\cdot}O{\cdot}CO{\cdot}C_{10}H_7$.

Temp.	16·5	56°	96°	133·5°
D^t_4 ...	1·0319	1·0031	0·9722	0·9429

Temp.	0°	3°	9·5°	16°	28°	54°	59°	99°	131·5°	156°	178°	190°
a_D ...	+1·46	1·82	2·82	3·68	5·04	7·82	8·26	10·84	12·50	13·18	13·66	13·94

Temp.	2·5°	11·5°	13°	16·5°	27°	65°	93°	131°	156°	178°	190°
a_{ye} ...	+1·78	3·08	3·44	3·80	5·22	9·08	10·84	13·00	13·78	14·32	14·58
a_{gr} ...	+1·50	2·98	3·40	3·90	5·76	10·36	12·06	14·82	15·66	16·28	16·64

Temp.	2·5°	11·5°	14°	16·5	27°	65°	92°	131°	156°	178°	
a_{vi} ...	−1·60	+1·90	2·76	3·78	7·30	16·56	21·20	27·00	28·46	30·8 (approx.)	

Temp.	0°	10°	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+1·40	2·78	3·99	6·27	8·39	9·96	11·25	12·57	13·67	14·42	15·11
$[a]^t_{ye}$...	1·29	2·78	4·19	6·63	8·71	10·28	11·61	13·00	14·19	15·05	15·84
$[a]^t_{gr}$...	1·04	2·65	4·45	7·44	9·88	11·88	13·53	14·97	16·18	17·12	17·97
$[a]^t_{vi}$ ...	−2·30	+1·30	4·86	10·71	15·52	19·63	23·13	26·64	29·43	31·69	33·82

d-β-*Octyl* 1-*Naphthoate*, $C_6H_{13}\cdot CHMe\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	20°	59°	93·5°	138·5°
D^t_4	1·0185	0·9904	0·9620	0·9280

Temp.	14°	16°	23°	58°	66°	100°	117°	132°	159	197°
α_D	+0·70	1·02	2·18	5·60	6·92	9·10	10·08	10·92	11·96	13·20

Temp.	16°	23°	60°	67°	102°	117°	132°	158°	197°
α_{ye}	+0·96	2·16	6·16	6·78	9·60	10·68	11·42	12·46	13·72

Temp.	7°	16°	23°	61°	65°	104°	117°	132°	158°	197°
α_{gr}	−1·10	+0·70	2·06	6·96	7·64	11·10	12·14	13·02	14·26	15·70

Temp.	6°	16°	23°	62°	64·5°	105°	117°	132°	158°	197°
α_{vi}	−6·50	−2·30	+0·64	11·60	12·36	19·68	21·56	23·40	26·24	29·00

Temp.	0°	10°	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$	−1·90	+0·05	1·67	4·18	6·22	8·01	9·56	10·93	12·17	13·19	14·20
$[\alpha]^t_{ye}$	−2·11	−0·15	+1·67	4·18	6·23	8·14	9·97	11·49	12·74	13·77	14·76
$[\alpha]^t_{gr}$	−2·77	−0·49	+1·47	4·48	6·97	9·23	11·28	13·06	14·46	15·72	16·90
$[\alpha]^t_{vi}$	−9·36	−4·48	−0·39	+5·88	11·34	15·75	19·68	23·26	26·18	28·97	31·25

d-β-*Decyl* 1-*Naphthoate*, $C_8H_{17}\cdot CHMe\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	16°	56·5°	94°	137°
D^t_4	1·0067	0·9776	0·9526	0·9144

Temp.	5°	10°	16°	18·5°	24°	31·5°	42°	54°	64°	89°	136°	141°	173°
α_D	−0·76	±0	+0·78	1·26	2·08	2·88	3·96	5·22	5·86	7·80	10·42	10·80	11·96

Temp.	5·5°	8°	16°	18·5°	24°	30·5°	40°	58°	61°	98°	119°	124°	142°	173°
α_{ye}	−0·86	−0·22	+0·76	1·22	2·00	2·92	3·88	5·56	5·84	8·70	10·28	10·40	11·26	12·40

Temp.	5°	8°	16°	18·5°	24°	31°	39°	59°	61°	99°	119°	130°	142°	173°
α_{gr}	−1·32	−0·60	+0·60	1·10	2·00	3·16	4·10	6·38	6·66	10·00	11·44	11·90	12·84	14·16

Temp.	6°	8°	16°	18·5°	25°	30°	39°	60°	100°	113°	119°	126°	141°
α_{vi}	−5·70	−4·42	−1·62	−0·90	+1·22	3·26	5·34	10·54	17·98	19·70	21·18	21·40	23·60

Temp.	0°	10°	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$	−1·57	−0·01	+1·41	3·84	5·78	7·49	9·04	10·48	11·71	12·75	13·4
$[\alpha]^t_{ye}$	−1·67	−0·01	+1·38	3·96	5·95	7·73	9·40	10·94	12·23	13·30	14·22
$[\alpha]^t_{gr}$	−2·36	−0·40	+1·30	4·29	6·63	8·70	10·61	12·33	13·88	15·15	16·22
$[\alpha]^t_{vi}$	−9·14	−3·66	−0·02	+5·86	10·81	15·03	18·91	22·30	25·48	28·55	31·53

d-β-*Undecyl* 1-*Naphthoate*, $C_9H_{19}\cdot CHMe\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	15·5°	59°	95·5°	141°
D^t_4	0·9944	0·9659	0·9366	0·9039

Temp.	7°	13°	17°	20°	21°	26·5°	37°	45°	76°	94°	145°	165°	194°
α_D	−0·36	+0·74	1·22	1·60	1·76	2·34	3·44	4·12	6·72	8·00	10·26	10·94	11·80

Temp.	8°	11·5°	17·5°	20°	21°	26·5°	35°	48°	74°	98°	145°	164°	176°	194°
α_{ye}	−0·42	+0·48	1·02	1·48	1·74	2·38	3·20	4·60	6·64	8·40	10·82	11·38	12·00	12·50

Temp.	8°	12°	17·5°	20°	21°	26·5°	35°	48·5°	74°	100°	145°	165°	175°	194°
α_{gr}	−0·72	+0·30	1·12	1·48	1·72	2·50	3·58	5·10	7·52	9·64	12·24	13·00	13·60	14·14

Temp.	8°	12°	17·5°	20°	21°	26°	34°	49°	55°	74°	101°	145°
α_{vi}	−4·22	−1·92	−0·20	+0·34	0·74	2·22	4·30	8·02	9·40	12·68	17·20	22·42

Temp.	165°	175°	194°
α_{vi}	23·86	24·94	26 (approx.)

Temp.	10°	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]^t_D$	+0·19	1·63	3·78	5·63	7·32	8·87	10·14	11·16	12·10	12·90
$[\alpha]^t_{ye}$	+0·19	1·63	3·89	5·79	7·52	9·16	10·55	11·71	12·74	13·93
$[\alpha]^t_{gr}$	−0·20	+1·55	4·23	6·44	8·45	10·33	11·88	13·27	14·45	15·61
$[\alpha]^t_{vi}$	−3·37	+0·45	6·14	10·47	14·36	18·15	21·42	24·19	26·62	28·77

d-γ-*Nonyl* 1-*Naphthoate*, $C_6H_{13}\cdot CHEt\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	21°	56°	94°	137°
D_4^t ...	1·0096	0·9841	0·9551	0·9221

Temp.	6°	10°	19·5°	31·5°	55°	93°	114°	139°	167°	191°
a_D ...	−25·92	−24·96	−22·60	−20·08	−15·78	−10·24	−7·96	−5·44	−3·12	−1·70

Temp.	5°	11°	19·5°	31°	57°	91°	112°	139°	167°	191°
a_{ye} ...	−27·68	−25·98	−23·78	−21·06	−16·58	−11·24	−8·50	−5·60	−3·26	−1·84
a_{gr} ...	−31·98	−30·06	−27·70	−24·42	−19·10	−13·06	−9·96	−6·50	−4·08	−2·44

Temp.	5°	11°	19·5°	30·5°	56°	91°	112°	139°	167°	191°
a_{vi} ...	−60·90	−56·80	−52·34	−46·46	−35·80	−23·78	−17·30	−11·32	−6·56	−3·8 (approx.)

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]_D^t$ ...	−22·23	−18·62	−15·39	−12·45	−9·86	−7·65	−5·74	−3·98	−2·58
$[a]_{ye}^t$ ...	−23·34	−19·63	−16·36	−13·26	−10·47	−8·02	−5·98	−4·18	−2·78
$[a]_{gr}^t$ ...	−27·29	−22·64	−18·86	−15·27	−12·22	−9·50	−7·05	−5·12	−3·51
$[a]_{vi}^t$ ...	−51·39	−41·94	−34·80	−28·18	−21·88	−16·25	−12·13	−8·47	−5·51

d-*Benzylmethylcarbinyl* 1-*Naphthoate*, $CH_2Ph\cdot CHMe\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	21°	64·5°	95°	134°
D_4^t ...	1·1161	1·0831	1·0599	1·0303

Temp.	8·5°	15·5°	79°	114°	126°	131°	148°	184°
a_D	+32·38	32·46	32·74	32·66	32·58	32·44	32·24	31·84

Temp.	7°	16°	79°	112°	133°	148°	185°
a_{ye} ...	+34·22	34·28	34·58	34·28	34·04	33·80	33·40

Temp.	7°	16°	79·5°	112°	133°	148°	185°
a_{gr} ...	+39·40	39·56	39·82	39·68	39·30	39·16	38·54
a_{vi} ...	+75·7	76·5	77·7	77·3	76·8	76·4	75·1

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]_D^t$ ...	+29·10	29·63	30·10	30·55	30·91	31·31	31·58	31·80	32·05
$[a]_y^t$ ...	30·74	31·35	31·84	32·28	32·61	32·86	33·09	33·33	33·58
$[a]_{gr}^t$ ...	35·56	36·14	36·69	37·18	37·62	38·01	38·28	38·53	38·77
$[a]_{vl}^t$ ...	68·67	70·24	71·46	72·51	73·38	74·10	74·67	75·14	75·60

d-β-*Butyl* 2-*Naphthoate*, $CHMeEt\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	17·5°	55·5°	94·5°	133°
D_4^t ...	1·0655	1·0383	1·0039	0·9744

Temp.	19·5°	45°	87°	121°	140°	177°
a_D ...	+53·40	43·06	40·28	36·20	34·00	30·70

Temp.	19·5	42°	87°	120°	141°	177°
a_{ye} ...	+56·14	50·94	42·36	38·30	35·60	32·14

Temp.	19·5°	44°	87°	120°	141°	177°
a_{gr} ...	+64·40	58·24	48·68	44·08	40·66	36·80

Temp.	19·5°	40°	87°	120°	141°
a_{vi} ...	+117·24	106·60	87·94	79·66	73·70

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]_D^t$ ...	+50·04	46·82	43·75	40·78	38·57	36·87	35·13	33·68	32·62
$[a]_{ye}^t$ ...	52·62	47·88	45·80	42·87	40·47	38·78	37·00	35·37	34·13
$[a]_{gr}^t$ ...	60·32	56·44	52·74	49·20	46·59	44·47	42·32	40·51	39·12
$[a]_{vi}^t$ ...	109·82	101·62	94·33	88·61	84·45	80·74	76·67	75·36	

d-β-*Hexyl* 2-*Naphthoate*, C_4H_9·CHMe·O·CO·$C_{10}H_7$.

Temp.	18·5°	59°	93°	134°					
D^t_4 ...	1·0402	1·0099	0·9812	0·9496					
Temp.	19·5°	45°	83°	129°	170°	193°			
a_D	+59·44	55·76	50·90	45·90	42·14	40·70			
Temp.	19·5°	28°	45°	83°	127°	170°	193°		
a_{ye}.....	+62·48	61·26	58·76	53·66	47·70	44·30	42·70		
a_{gr}.....	+72·02	70·54	67·74	61·32	55·04	50·92	49·36		
Temp.	19·5°	28°	45°	83°	129°	170°	193°		
a_{vi}....	+132·68	130·12	125·22	113·60	100·00	94·00	91·32		
Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+57·11	55·30	53·60	51·82	50·19	48·75	47·54	46·03	45·62
$[a]^t_{ye}$ ...	60·00	58·22	56·38	54·48	52·57	50·82	49·53	48·57	47·81
$[a]^t_{gr}$ ...	69·16	66·97	64·69	62·36	60·28	58·36	56·92	55·95	55·16
$[a]^t_{vi}$ ...	127·44	123·81	119·84	115·71	111·25	106·98	103·90	102·64	102·00

d-β-*Octyl* 2-*Naphthoate*, C_6H_{13}·CHMe·O·CO·$C_{10}H_7$.

Temp.	19°	53·5°	91·5°	136·5°					
D^t_4 ...	1·0144	0·9874	0·9595	0·9253					
Temp.	9°	20°	21°	24°	65°	120°	159°	188°	
a_D	+58·20	57·10	56·88	56·68	53·10	48·58	46·40	43·90	
Temp.	8°	18°	21°	24°	70°	119°	159°	188°	
a_{ye} ...	+61·80	60·08	59·78	59·24	55·16	50·76	48·40	46·06	
Temp.	6°	18°	22°	24°	71·5°	119°	159°	188°	
a_{gr}.....	+71·00	69·26	68·90	68·68	63·46	58·44	55·66	53·16	
Temp.	7°	18°	22°	24°	69°	119°	159°	188°	
a_{vi}	+131·50	128·12	126·86	126·60	117·50	107·96	102·50	98·60	
Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+56·25	55·17	54·30	53·51	52·77	51·97	51·33	50·71	49·37
$[a]^t_{ye}$...	58·99	57·82	56·87	55·99	55·20	54·46	53·68	52·92	51·41
$[a]^t_{gr}$ ...	68·11	66·80	65·66	64·60	63·49	62·48	61·78	61·03	59·42
$[a]^t_{vi}$ ...	125·84	123·25	120·86	118·85	116·91	115·06	113·77	112·81	109·00

d-β-*Undecyl* 2-*Naphthoate*, C_9H_{19}·CHMe·O·CO·$C_{10}H_7$.

Temp.	21°	58·5°	95·5°	133°					
D^t_4 ...	0·9898	0·9623	0·9334	0·9069					
Temp.	20°	58°	87°	123°	149°	193°			
a_D.....	+49·56	47·16	45·36	43·06	41·80	39·40			
Temp.	20°	61°	87°	124·5°	149°	193°			
a_{ye} ...	+52·16	49·40	47·66	45·06	43·90	41·24			
Temp.	20°	59°	87°	125°	149°	193°			
a_{gr} ...	+60·16	57·14	54·90	51·90	50·40	47·54			
Temp.	20°	66°	87°	125°	149°				
a_{vi} ...	+111·20	104·40	101·40	95·78	93·46				
Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[a]^t_D$ ...	+50·03	49·54	49·03	48·45	47·89	47·29	46·84	46·47	46·00
$[a]^t_{ye}$...	52·66	52·10	51·50	50·86	50·24	49·55	49·13	48·71	48·18
$[a]^t_{gr}$...	60·72	60·08	59·37	58·63	57·87	57·09	56·46	55·94	55·42
$[a]^t_{vi}$...	112·36	110·99	109·62	108·24	106·77	105·31	104·48	104·44	—

d-γ-*Nonyl* 2-*Naphthoate*, $C_6H_{13}\cdot CHEt\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	19°	55°	91°	129°
D_4^t ...	1·0054	0·9829	0·9510	0·9238

Temp.	21°	37°	76°	106°	128°	148°	168°	185°
α_D.....	+19·30	20·04	21·80	22·48	22·80	22·96	22·90	22·98

Temp.	21°	39°	72°	106°	128°	148°	168°	185°
α_{ye}.....	+20·20	21·34	22·76	23·60	24·00	24·20	24·18	24·22
α_{gr}	+23·50	24·62	26·38	27·24	27·62	27·82	27·84	27·90

Temp.	21°	39°	70°	106°	126°	148°	168°	185°
α_{vi}... ...	+44·92	46·86	50·14	51·80	52·26	52·44	52·30	52·48

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]_D^t$ ...	+19·14	20·33	21·68	22·84	23·68	24·37	25·00	25·06	25·92
$[\alpha]_{ye}^t$...	+20·04	21·48	22·79	23·92	24·83	25·61	26·39	26·86	27·32
$[\alpha]_{gr}^t$ ...	+23·30	24·91	26·46	27·68	28·65	29·53	30·33	30·89	31·49
$[\alpha]_{vi}^t$ ...	+44·54	46·93	50·22	52·91	54·62	55·99	57·21	58·20	59·21

d-*Benzylmethylcarbinyl* 2-*Naphthoate*, $CH_2Ph\cdot CHMe\cdot O\cdot CO\cdot C_{10}H_7$.

Temp.	26°	60°	94°	139°
D_4^t ...	1·1076	1·0818	1·0549	1·0214

Temp.	21°	46°	61°	73°	97°	137°	175°	197°
α_D.....	+136·16	126·90	121·88	118·60	111·76	102·70	95·48	91·60

Temp.	21°	46°	60°	70°	97°	137°	178°	197°
α_{ye} ...	+143·08	132·74	128·64	125·50	118·10	107·90	99·84	96·46

Temp.	21°	46°	59°	69°	97°	137°	178°	197°
α_{gr} ...	+166·16	154·54	149·54	146·08	136·92	125·54	115·96	111·68
α_{vi} (approx.)	+321·9	300·2	289·2	283·3	266·0	241·8	223·4	217·6

Temp.	20°	40°	60°	80°	100°	120°	140°	160°	180°
$[\alpha]_D^t$ ...	+122·83	117·71	112·98	109·38	105·81	102·82	99·94	97·51	95·41
$[\alpha]_{ye}^t$ ...	129·04	123·54	118·90	114·90	111·62	108·13	105·23	102·49	100·56
$[\alpha]_{gr}^t$ ...	149·82	143·32	137·94	133·66	129·42	125·51	122·28	119·40	116·44
$[\alpha]_{vi}^t$ ...	290·2	278·2	267·5	259·1	251·2	243·1	235·7	229·7	225·0

Table III.

Determinations of Rotatory Power in (approx.) 5 per cent. Solutions.

Solvent.	Length of tube, cm.	Weight of solute in grams.	α_D.	α_{ye}.	α_{gr}.	α_{vi}.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.
d-β-*Butyl Benzoate.*														
Ethyl alcohol	20	1·0739	+4·32°	+4·53°	+5·16°	+8·65°	+40·23°	+42·18	+48·04°	+80·54°	+71·6°	+75·1°	+85·5°	+143·3°
Carbon disulphide	10	1·0350	2·09	2·18	2·49	4·24	40·38	42·13	48·11	81·94	71·9	75·0	85·7	145·8
d-β-*Hexyl Benzoate.*														
Ethyl alcohol	20	1·1299	+4·63	+4·85	+5·55	+9·53	+40·98	+42·91	+49·11	+84·33	+84·4	+88·4	+101·2	+173·8
Carbon disulphide	22	1·0105	3·55	3·70	4·24	7·16	31·93	33·28	38·14	64·39	65·8	69·6	78·6	132·6
d-β-*Octyl Benzoate.*														
Pyridine	20	0·9828	+2·50	+2·64	+3·07	+5·15	+25·43	+26·86	+31·23	+52·40	+59·5	+62·9	+73·1	+121·7
Benzene	22	0·9538	2·96	3·12	3·59	6·13	28·21	29·74	34·22	58·40	66·0	69·6	80·1	136·8
Carbon disulphide	22	1·0571	3·45	3·64	4·12	7·13	29·68	31·31	35·44	61·34	69·4	73·3	82·9	143·5
Chloroform	22	0·9891	3·78	3·96	4·49	7·70	34·74	36·40	41·27	70·78	81·3	85·2	96·6	165·6
Ethyl alcohol	20	0·9908	3·89	4·07	4·69	8·12	39·26	41·09	47·35	82·54	91·9	96·1	110·8	193·0
Ethyl acetate	20	1·0228	4·25	4·43	5·13	8·82	42·51	44·31	51·31	88·22	99·5	103·7	120·0	206·5
d-γ-*Nonyl Benzoate.*														
Ethyl alcohol	10	0·9990	+0·60	+0·66	+0·74	+1·33	+12·01	+13·21	+14·85	+26·63	+29·8	+32·8	+36·7	+66·0
Carbon disulphide	20	1·0414	0·13	0·17	0·19	0·36	1·25	1·63	1·83	3·46	3·1	3·2	4·5	8·6

Solvent	Length of tube, cm.	Weight of solute in grams.	α_D.	$\alpha_{ye.}$	$\alpha_{gr.}$	$\alpha_{vi.}$	$[\alpha]_D$.	$[\alpha]_{ye.}$	$[\alpha]_{gr.}$	$[\alpha]_{vi.}$	$[M]_D$.	$[M]_{ye.}$	$[M]_{gr.}$	$[M]_{vi.}$
d-*Benzylmethylcarbinyl Benzoate.*														
Ethyl alcohol	10	1·1351	+4·00°	+4·25°	+4·93°	+8·90°	+70·49°	+74·89°	+86·86°	+156·8°	+169·1°	+179·7°	+208·4°	+376·3°
Carbon disulphide	22	1·0141	7·75	8·15	9·49	17·62	69·49	73·08	85·09	158·0°	166·7	175·4	204·2	379·1
.....														
.....														
d-*β-Octyl* 1-*Naphthoate.*														
Benzene	20	1·0105	+0·80	+0·85	+0·95	+1·90	+7·92	+7·97	+9·40	+18·80	+22·5	+22·6	+26·7	+53·4
Pyridine	22	1·1120	0·97	1·04	1·18	2·28	8·72	9·35	10·61	20·50	24·8	26·6	30·1	58·2
Carbon disulphide	22	1·0592	1·27	1·34	1·48	2·97	10·90	11·50	12·70	25·49	31·0	32·7	36·1	72·4
Chloroform	20	1·0195	1·66	1·75	1·99	3·54	16·28	17·17	19·52	34·72	46·2	48·8	55·4	98·6
Ethyl alcohol	20	1·1588	2·19	2·35	2·63	4·69	18·90	20·27	22·70	40·47	53·7	57·6	64·5	114·9
Ethyl acetate	20	1·1015	2·16	2·29	2·58	4·50	19·61	20·89	23·42	40·85	55·7	59·0	66·5	116·0
d-*γ-Nonyl* 1-*Naphthoate.*														
Ethyl alcohol	10	1·0429	−0·14	−0·16	−0·16	−0·38	−2·69	−3·07	−3·07	−7·29	−8·0	−9·1	−9·1	−21·7
Carbon disulphide	20	1·2452	−1·87	−1·91	−2·25	−3·86	−15·00	−15·34	−18·07	−31·00	−44·8	−45·7	−53·9	−93·4
d-*Benzylmethylcarbinyl* 1-*Naphthoate.*														
Ethyl alcohol	20	1·0186	+3·67	+3·83	+4·35	+8·09	+36·02	+37·59	+42·70	+79·39	+104·5	+109·0	+123·8	+230·2
Carbon disulphide	20	1·0494	4·69	4·90	5·70	11·30	44·71	46·71	54·34	107·70	129·6	135·5	157·6	312·4

Solvent.	Length of tube, cm.	Weight of solute in grams	α_D.	α_{ye}.	α_{gr}.	α_{vi}.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{ye}$.	$[M]_{gr}$.	$[M]_{vi}$.
d-β-*Octyl* 2-*Naphthoate*.														
Ethyl alcohol	20	1·0697	+5·83°	+6·14°	+7·08°	+12·95°	+45·58°	+48·00°	+55·35°	+101·24°	+129·4°	+136·3°	+157·2°	+287·5°
Chloroform	22	1·0702	5·76	5·98	6·90	12·60	48·93	50·80	58·61	107·04	139·0	144·3	166·5	304·0
Pyridine	20	1·1353	5·68	5·99	6·91	12·78	50·03	52·76	60·87	112·57	142·1	150·5	172·9	319·7
Benzene	20	1·0042	5·33	5·65	6·49	11·99	53·08	56·26	64·63	119·40	150·7	159·8	183·5	339·1
Carbon disulphide	22	1·1256	6·92	7·29	8·41	15·84	55·89	58·88	67·93	127·94	158·7	167·2	192·9	363·3
Ethyl acetate	20	1·1688	6·89	7·25	8·35	15·20	58·95	62·03	71·44	130·05	167·4	176·2	202·9	369·3
d-γ-*Nonyl* 2-*Naphthoate*.														
Ethyl alcohol	10	1·1230	+1·50	+1·60	+1·83	+3·55	+26·71	+28·49	+32·59	+63·23	+68·4	+72·9	+83·4	+165·6
Carbon disulphide	20	1·1247	2·56	2·69	3·16	6·16	22·76	23·92	28·09	54·76	58·3	61·2	71·9	140·2
d-*Benzylmethylcarbinyl* 2-*Naphthoate*.														
Ethyl alcohol	10	1·0364	+6·63	+6·92	+8·00	+15·45	+127·9	+133·6	+155·4	+298·2	+371·1	+387·4	+447·8	+864·8
Carbon disulphide	22	0·9725	14·05	14·78	17·15	33·75	131·3	138·1	160·3	315·4	380·8	399·9	464·9	914·7

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has defrayed some of the expense of this investigation.

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XIV.—*α-Hydroxy-β-phenylcrotonolactone.*

By NORMAN HALL, JAMES EDWARD HYNES, and ARTHUR LAPWORTH.

DURING the course of experiments for which considerable quantities of phenylpyruvic acid, $C_6H_5\cdot CH_2\cdot CO\cdot CO_2H$, were required, the authors attempted to prepare this compound from α-oximino-β-phenylpropionic acid, $CH_2Ph\cdot C(:NOH)\cdot CO_2H$, which can readily be obtained from benzylacetoacetic ester. By heating the oximino-compound with formaldehyde and hydrochloric acid (compare Lapworth, T., 1907, **91**, 1133) an acid was obtained which was free from nitrogen, and gave a green coloration with ferric chloride, closely resembling that which phenylpyruvic acid displays in similar circumstances. On further examination this acid was found to have the formula $C_{10}H_8O_3$, and had evidently been produced by the condensation of formaldehyde with phenylpyruvic acid, formed in the first stage, and in accordance with the equation:

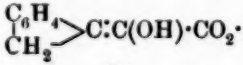
$$C_9H_8O_3 + CH_2O = C_{10}H_8O_3 + H_2O.$$

The authors considered the possibility of representing the acid as the methylene derivative of phenylpyruvic acid, produced in the following way:

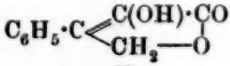
$$C_6H_5\cdot CH_2\cdot CO\cdot CO_2H + CH_2O = C_6H_5\cdot C(:CH_2)\cdot CO\cdot CO_2H + H_2O,$$

but rejected it as inconsistent with the behaviour of the compound towards ferric chloride, for the intense coloration it gives with that reagent is displayed by such ketonic acids only as are capable of reacting in the enolic form, $CXY{:}C(OH)\cdot CO_2H$, from which the highly-coloured ferric compounds are derived. The complete absence of ketonic properties shown by the acid and its derivatives was also not easily to be explained by the formula.

No enolic modification of the formula of phenylmethylenepyruvic acid can be devised in which both the free phenyl group and the free carboxyl group are present; but if the assumption be made that one or other of these has disappeared, then the following forms present themselves:



(I.)



(II.)

Of these, I, if written in full, represents three different compounds, which on oxidation would yield the three phthalic acids. The new compound, however, yields only benzoic acid and other products containing the phenyl group as such.

Formula II at first appeared difficult to reconcile with the considerable acidity manifested by the new substance, which dissolves in cold aqueous sodium carbonate, and may even be titrated with standard sodium hydroxide, using phenolphthalein as indicator. It was observed, however, that the end-reaction in the latter instance was not quite sharp, and that the acid could be precipitated from the aqueous solution of the sodium salt by excess of carbon dioxide. These observations excluded the possibility of representing the compound as an α-hydroxy- or α-ketonic-carboxylic acid, and recalled the properties of compounds, such as tetronic acid and *iso*-oxazalones, which contain the group $>C{:}C(OH)\cdot$ as a portion of a ring, as in formula II above. The latter formula therefore accounts fully for the acid properties of the new compound, its reaction with ferric chloride, and its formation from formaldehyde and phenylpyruvic acid. This synthesis may be represented as follows:

$$C_6H_5\cdot CH_2\cdot CO\cdot CO_2H + CH_2O \longrightarrow C_6H_5\cdot CH\begin{matrix}CO\cdot CO_2H\\ CH_2\cdot OH\end{matrix} \longrightarrow$$

$$H_2O + C_6H_5\cdot CH\begin{matrix}CO\text{—}CO\\ CH_2\cdot O\end{matrix},$$

where the last formula is the ketonic modification of II.

On applying the method devised by K. Meyer for the estimation of the proportion of enol in such substances it was found that in alcoholic solution this compound instantaneously absorbed only 0·9 gram-molecule of bromine. The authors are disposed to believe that this case is one in which that particular method fails in accuracy; the instantaneous absorption of so much halogen certainly provides strong evidence that a considerable proportion of enol is present, but the bromo-derivative formed is here an unstable one, and readily loses hydrogen bromide, as the authors discovered on attempting to isolate it. In such cases the quantity of iodine liberated in the last step in Meyer's process will be too small, and the proportion of enol as calculated from the titration will be too low; for this reason the number 0·9 must be taken as the lower limit for the proportion of enol in alcoholic solution; further, since ketonic properties are wholly absent, the authors consider it practically certain that the solid compound is the pure enol, or *α-hydroxy-β-phenylcrotonolactone.*

The compound reacts readily with acyl chlorides, a fact which strengthens the view that the lactone has the enolic structure. The acyl derivatives do not discharge the colour of bromine or perman-

ganate in the cold, and were at first believed to be *C*-substitution derivatives of the type $C_6H_5\cdot C(CO\cdot CH_3)\begin{matrix}CO-CO\\ CH_2\cdot O\end{matrix}$; they fail, however, to respond to any of the tests for ketones, and readily lose their acyl groups, so that they must be recognised as true *O*-derivatives of the enol-lactone. The inactivity of the ethylenic linking towards bromine is not confined to derivatives of this lactone, and is doubtless due to its conjugation with the carbonyl group, as in $\alpha\beta$-unsaturated acids; the latter react with bromine abnormally slowly, and in certain instances with inappreciable speed at the ordinary temperature.

The sodium derivative of the lactone is readily acted on by alkylating agents. The alkyl derivatives resemble the acyl compounds in their behaviour towards bromine and permanganate, but, like these, are to be recognised as *O*-substitution products. They give negative results when tests for ketones are applied to them, they are attacked (although slowly) by ozone, and in their absorption spectra closely resemble the original lactone.

Although the lactone is very readily attacked by potassium permanganate, the oxidation proceeds too far to be of service in throwing light on the structure of that substance. The reaction with hydrogen peroxide, however, offers unequivocal evidence in favour of the views advanced above. In neutral, acid, or alkaline solution the products are oxalic acid and benzoylcarbinol; probably the hydrogen oxalate of benzoylcarbinol is an intermediate product, in which case the course of the oxidation process is very clear:

$$C_6H_5\cdot C\begin{matrix}C(OH)\cdot CO\\ CH_2-O\end{matrix} \rightarrow C_6H_5\cdot C\begin{matrix}O\ O:C(OH)\cdot CO\\ CH_2\qquad\quad O\end{matrix} \rightarrow$$

$$C_6H_5\cdot C\begin{matrix}O\\ CH_2\cdot OH\end{matrix} + H_2C_2O_4.$$

When hydroxyphenylcrotonolactone is heated, carbon monoxide and dioxide are evolved, and a mixture of atropic acid and a neutral oil, which is almost certainly styrene, is formed. The reactions are readily followed if the assumption be made that the lactone is first converted in the isodynamic phenylmethylenepyruvic acid:

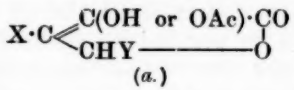
$$C_6H_5\cdot C\begin{matrix}C(OH)\cdot CO\\ CH_2-O\end{matrix} \rightarrow$$

$$C_6H_5\cdot C\begin{matrix}CO\cdot CO_2H\\ CH_2\end{matrix} \rightarrow C_6H_5\cdot C\begin{matrix}CO_2H\\ CH_2\end{matrix} + CO$$

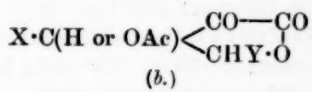
$$\rightarrow C_6H_5\cdot CH:CH_2 + CO + CO_2$$

Erlenmeyer, jun., and his pupils have described a number of compounds similar to those described in the present paper, having

obtained them from phenylpyruvic acid by condensation with aromatic aldehydes (*Ber.*, 1894, **27**, 2222; 1898, **31**, 2218; 1902, **35**, 1935; 1903, **36**, 919, 2344; *Annalen*, 1904, **333**, 228, 268). By condensing either piperonaldehyde or cuminaldehyde with phenylpyruvic acid, two isomeric lactones were apparently obtained, each of which yielded a distinct acetyl and benzoyl derivative. These isomerides were very similar, and it was concluded that they were simply stereoisomerides; the enolic formulation (*a*) which does not admit of the existence of such isomerides, was therefore abandoned in favour of the ketonic one (*b*), of which there are two stereoisomeric modifications.



(*a.*)



(*b.*)

The properties of the compounds discussed by Erlenmeyer do not appear to differ in any essential respect from those possessed by the substances dealt with in the present communication; consequently, either formula (*a*) or (*b*) must be applied uniformly to both series. Thus it is clear that Erlenmeyer's theory is opposed to that here advocated, and as the former has priority in respect of date it cannot be dismissed without comment. The present authors consider that the evidence adduced in favour of (*b*) is unsatisfactory in comparison with that for (*a*), and venture to point out that if Erlenmeyer's view be accepted, then it must be concluded that enolisation does not take place when the lactones of this series are converted into acyl derivatives, otherwise the isomeric lactones would yield identical products for the enolic forms themselves are identical; in other words, acyl chlorides, even in the cold, effect the direct replacement by an acyl group of a hydrogen atom attached to carbon, which is a conclusion hardly to be admitted at the present time.

On the other hand, there is no simple explanation which covers all the data as they at present appear, and the whole matter of isomerism in the series, (*a*) and (*b*) above, seems worthy of re-investigation.

Experimental.

Ethyl α-oximino-β-phenylpropionate, $CH_2Ph·C(:NOH)·CO_2H$, may be prepared by Dieckmann's process (*Ber.*, 1900, **33**, 586) or by that of Bouveault and Locquin (*Bull. Soc. Chim.*, 1904, [iii], **31**, 1142). The following modification of the latter process is to be recommended.

A solution of nitrosylsulphuric acid is prepared by passing nitrous fumes from arsenious oxide and nitric acid into concen-

trated sulphuric acid, until crystals separate permanently; these are dissolved by the addition of a little more sulphuric acid, and the resulting solution is standardised by means of the nitrometer. Benzylacetoacetic ester (1 mol.) is cautiously dissolved in an equal weight of cold sulphuric acid to which about 10 per cent. of water has been added; to this is then introduced, in small quantities at a time, nitrosylsulphuric acid solution (1 mol. of $NO_2 \cdot SO_3H$), while the temperature is kept at about 15°. (The presence of the water in the acid has been found to facilitate the reaction considerably.) As soon as the temperature of the mixture shows no tendency to rise (ten to fifteen minutes), the whole is poured on powdered ice, with constant stirring, and allowed to remain until the oil has solidified; the oximino-ester may then be purified as directed by previous workers. The yield is 70—80 per cent. of that theoretically possible.

If the free acid is required, the crude ester may at once be dissolved in fifteen times its weight of 20 per cent. potassium hydroxide, the solution boiled for some hours, then for some minutes with the addition of animal charcoal, cooled, filtered, and acidified. The acid is collected, washed with chloroform to remove phenylpropionic acid, and crystallised from dilute alcohol. The yield, if the crude ester is employed, is at least 75 per cent. of that theoretically possible.

Formation of α-Hydroxy-β-phenylcrotonolactone,

$$C_6H_5 \cdot C \begin{matrix} C(OH) \cdot CO \\ CH_2 — O \end{matrix} .$$

α-Oximino-β-phenylpropionic acid (50 grams) is added to a mixture of 40 per cent. formaldehyde (500 grams) and concentrated hydrochloric acid (500 grams), and the whole heated to boiling. The solid dissolves, and after a few minutes a precipitate appears; when this no longer increases in amount the whole is cooled and the deposit collected, and purified by crystallisation from dilute alcohol. It was not found advantageous to attempt to obtain any more by any treatment of the mother liquors. The yield of purified compound was 40—50 per cent. of the theoretical amount.

α-Hydroxy-β-phenylcrotonolactone is practically insoluble in chloroform, benzene, or light petroleum, very sparingly soluble in ether or cold water, but dissolves freely in hot ethyl acetate, acetone, or alcohol, and crystallises from these in small, colourless needles, which melt and decompose slightly at 197—198°. It may also be crystallised from much hot water:

Found: C = 68·2; H = 4·6.

$C_{10}H_8O_3$ requires C = 68·2; H = 4·6 per cent.

0·2008 Gram required 11·8 c.c. of *N*/10-NaOH for neutralisation,

using phenolphthalein as indicator, the end-point being somewhat indefinite, however; the equivalent was thus roughly 178, which is that required for a monobasic acid, $C_{10}H_8O_3$.

An alcoholic solution of the acid gives with ferric chloride an intense green coloration, which is discharged by the addition of water, and with a trace of cupric acetate a brown colour, which becomes green on the addition of more copper salt.

A solution of the substance in alcohol or acetic acid at once discharges the colour of bromine, and an aqueous solution instantaneously decolorises faintly alkaline permanganate.

The compound dissolves freely in aqueous sodium hydroxide or carbonate, forming a pale yellow solution, from which it is reprecipitated almost quantitatively by carbon dioxide. The solution of the sodium salt gives almost white precipitates on addition of calcium, cobalt, barium, or mercuric chloride, and these, in the last two instances, are soluble on boiling; with silver nitrate a white precipitate is formed, which almost immediately turns yellow, and, when warmed, becomes black, whilst a mirror appears on the containing vessel. Ferrous sulphate gives a yellow precipitate, which gradually turns black.

The *sodium* and *potassium* salts may be prepared by dissolving the acid in warm concentrated aqueous solutions of the corresponding carbonates, and, on cooling, separate in white needles. The pure salts form alkaline solutions.

When hydroxyphenylcrotonolactone is boiled with excess of baryta-water it is slowly decomposed, and a powerful odour resembling phenylacetaldehyde becomes perceptible. If the issuing steam is condensed the water is seen to contain only globules in suspension, and responds to the usual tests for aldehydes. The oil appeared to consist mainly of styrene.

Phosphorus pentachloride, trichloride, phosphoryl chloride, and thionyl chloride attack the lactone only with great difficulty, but if ethyl acetate is present the pentachloride reacts in the cold, and the lactone, at first insoluble, rapidly dissolves, forming a clear solution, which then deposits a white, micro-crystalline solid. The latter contained both phosphorus and chlorine, was insoluble in all the usual media, and could not be obtained uniform in composition; it dissolved slowly in dilute aqueous alkalis, the original lactone being formed.

Application of K. Meyer's Method to Hydroxyphenylcrotonolactone.

Several attempts were made to determine the percentage of enol in the lactone by this process (compare *Annalen*, 1911, **380**, 212 *et seq.*, and *Ber.*, 1911, **44**, 2718, etc.). In one instance, 0·25 gram

of the compound was used, and 26·5 c.c. of 0·995*N*-thiosulphate were required to discharge the colour of the iodine liberated in the latter step of the procedure, a result corresponding with a conversion of 92 per cent. of the lactone into monobromo-derivative. Although other estimations gave results roughly in agreement with this, reasons have already been given for believing that the true percentage of enol is higher than this number suggests.

All attempts to obtain hydrazones, a semicarbazide, or an oxime from the lactone resulted in the latter being recovered unchanged.

Action of Acyl Chlorides on α-Hydroxy-β-phenylcrotonolactone.

Acetyl Derivative, $C_6H_5\cdot C\begin{matrix}C(OAc)\cdot CO\\ CH_2\text{——}O\end{matrix}$.

The lactone reacts with excess of acetyl chloride in the cold, and with great readiness in the presence of a trace of concentrated sulphuric acid. The solid dissolves, and crystals are subsequently deposited, which may be collected, drained on porous earthenware, and recrystallised from warm ethyl acetate:

Found: C = 66·2; H = 4·8.

$C_{12}H_{10}O_4$ requires C = 66·0; H = 4·6 per cent.

This *acetyl* derivative dissolves somewhat readily in chloroform, ethyl acetate, or acetone, sparingly in light petroleum, and separates from ethyl acetate in transparent, colourless plates, melting at 138—140°. When warmed with aqueous alkali it dissolves very slowly, undergoing hydrolysis, and forming a yellow solution similar to that obtained by dissolving the original lactone in alkalis; when warmed with sulphuric acid and alcohol, the compound yields ethyl acetate.

Unlike the original lactone, the acetyl derivative does not decolorise bromine in alcohol, at least in the cold, and it is somewhat stable in acetone solution towards potassium permanganate. It is attacked exceedingly slowly, if at all, by dry ozone in chloroform solution, but in the presence of moisture oxidation occurs to some extent, although the products have not been isolated.

Phenylhydrazine acts on the acetyl compound, slowly at the ordinary temperature and rapidly on heating; the acetyl group is eliminated, and the original lactone is deposited in crystals.

Benzoyl Derivative, $C_6H_5\cdot C\begin{matrix}C(OBz)\cdot CO\\ CH_2\text{——}O\end{matrix}$.

When α-hydroxy-β-phenylcrotonolactone is dissolved in excess of dilute aqueous sodium hydroxide and the cooled solution then shaken with benzoyl chloride, a portion is converted into the

benzoyl derivative, which separates as an oil, and subsequently solidifies. The conditions for obtaining good yields of this derivative have not been discovered.

The dried neutral product may be crystallised from a mixture of chloroform and petroleum.

Found: C = 73·0; H = 4·5.

$C_{17}H_{12}O_4$ requires C = 72·8; H = 4·3 per cent.

The substance resembles the acetyl derivative in regard to its solubilities in organic media and in alkalis, and it does not discharge the colour of a solution of bromine in alcohol, nor does it readily absorb dilute ozone in chloroform solution. It crystallises in needles or plates, and melts at 146—148°.

The substance is hydrolysed with hot alkalis, and when it is warmed with alcohol containing sulphuric acid the odour of benzoic ester becomes perceptible.

Action of Alkylating Agents on α-Hydroxy-β-phenylcrotonolactone. Methyl Derivative, $C_6H_5 \cdot C \lessdot \begin{matrix} C(OMe) \cdot CO \\ CH_2 \text{——} O \end{matrix}$.

When the lactone was converted into its sodium derivative, the latter dried and warmed with methyl sulphate in methyl-alcoholic solution, a neutral oil was obtained, which did not crystallise. When Erlenmeyer's method was used, however, the product was at once obtained in a crystalline condition; in this instance one atomic proportion of sodium was dissolved in absolute methyl alcohol, the solution then added to a solution of the lactone (one molecular proportion) in the same solvent, methyl iodide being subsequently introduced and the whole boiled until all alkalinity had disappeared. On evaporation of the solvent and addition of water to the residue, the methyl derivative remained as a solid, and was washed, dried, and crystallised from alcohol.

Found: C = 69·2; H = 5·3.

$C_{11}H_{10}O_3$ requires C = 69·5; H = 5·3 per cent.

This substance crystallises in yellow needles, which melt at 81·5°. It dissolves somewhat freely in the usual organic media, but is nearly insoluble in light petroleum. Like the acyl derivatives of hydroxyphenylcrotonolactone, it does not at once discharge the colour of bromine in dilute alcoholic solution.

The corresponding *benzyl* derivative, $C_{17}H_{14}O_3$, is readily prepared by a method precisely similar to that employed for the methyl derivative, benzyl chloride being substituted for methyl iodide. It crystallises in lustrous, faintly yellow plates, melting at 69·5°.

Found: C = 76·5; H = 5·3.

$C_{17}H_{14}O_3$ requires C = 76·7; H = 5·2 per cent.

In its chemical properties it closely resembles the corresponding acetyl derivative.

Thermal Decomposition of α-Hydroxy-β-phenylcrotonolactone. Formation of Atropic Acid.

When the lactone is heated at 220° it decomposes slowly, darkening, and evolving a mixture of approximately equal volumes of carbon monoxide and carbon dioxide, whilst a small sublimate of unchanged acid is formed. If the residue is subsequently distilled under the atmospheric pressure, a yellow liquid passes over, which slowly deposits a small quantity of a solid acid, and this may be purified by crystallisation from alcohol (Found, C = 73·2; H = 5·0. $C_9H_8O_2$ requires C = 72·9; H = 5·4 per cent.).

0·1464 Gram required 7·9 c.c. of 0·124*N*-NaOH for complete neutralisation, using phenolphthalein as indicator; equivalent = 149. The equivalent of a monobasic acid, $C_9H_8O_2$, is 148.

The acid separated from alcohol in elongated, glistening plates, melting at 106°, and thus closely resembled atropic acid. It was therefore compared with a pure sample of synthetic atropic acid, and was found to be identical with it.

A neutral oil accompanies atropic acid in the above distillate, and although the quantity of this was too small for complete identification its odour and general characters were those of styrene.

Oxidation of α-Hydroxy-β-phenylcrotonolactone. Formation of Benzoylcarbinol.

On oxidation of the lactone by potassium permanganate the final products are benzoic acid and oxalic acid, and it is difficult to arrest the process at an intermediate stage. The action of hydrogen peroxide, on the other hand, is easily regulated.

A solution of the lactone in aqueous sodium carbonate was slowly mixed with enough hydrogen peroxide (30 per cent.) to discharge the faint yellow colour of the former. Manganese dioxide was then added, and when the evolution of oxygen had ceased the solution was filtered, acidified, and extracted with ether. Oxalic acid was easily detected in the aqueous portion, and the ethereal extract yielded on evaporation a solid mass, which was resolved by fractional crystallisation into benzoic acid and a substance which separated from ether in large, transparent prisms, melting at 86°.

The latter compound was acidic in character. When heated alone or with alkalis it yielded benzaldehyde, and was converted

by benzoyl chloride and alkali into a neutral, crystalline benzoyl derivative, which melted at 117°. When warmed with a solution of phenylhydrazine acetate it gave a sparingly soluble phenylhydrazone, which crystallised from ethyl acetate in yellow needles, melting at 111° (Found, C = 74·5 *; N = 12·6. $C_{14}H_{14}ON_2$ requires C = 74·3; N = 12·4 per cent.).

The second oxidation product from α-hydroxy-β-phenylcrotonolactone was thus identified as benzoylcarbinol.

The oxidation of the lactone can also be carried out in acetic acid solution with hydrogen peroxide (30 per cent.) at 40—50°, and if the conditions are favourable benzoylcarbinol may separate in well-defined needles.

Reduction of α-Hydroxy-β-phenylcrotonolactone. Formation of α-Hydroxy-β-phenylbutyrolactone, $C_6H_5 \cdot CH\begin{matrix}CH(OH)\cdot CO\\ CH_2 \text{——} O\end{matrix}$.

The lactone was not reduced when heated with hydriodic acid at 125—170° for several hours. It was also not attacked by all the ordinary methods for reduction by gaseous hydrogen in the presence of colloidal platinum or palladium, at pressures up to two atmospheres.

It is rapidly reduced, however, when the aqueous solution of the sodium salt is shaken with clean liquid sodium amalgam. When the resulting solution is acidified there is no precipitate, nor can the reduction products be extracted by any of the common liquids used for such purposes. On keeping, however, the solution becomes turbid, and an oil separates which may be dissolved in methyl ethyl ketone. The latter on evaporation leaves a viscid liquid, which slowly deposits crystals, and these can be drained on porous earthenware and crystallised from a variety of solvents.

The new hydroxy-lactone crystallises from alcohol, ether, or methyl ethyl ketone in prisms which melt at 99°; from ether or from a mixture of benzene and light petroleum it frequently appears in needles, which melt at 88—90°, and both types were analysed:

Needles from ether. Found: C = 67·1; H = 5·6.
Prisms from methylethylketone. Found: C = 67·0; H = 5·5.
$C_{10}H_{10}O_3$ requires C = 67·4; H = 5·6 per cent.

On addition of sodium ethoxide to an alcoholic solution of the lactone, a *sodium* salt, melting at 258—259°, separates in crystalline form. The lustrous plates dissolve readily in water, and on

* Unfortunately no record was kept of the precise percentage of hydrogen found, but at the time the analysis was made the number was considered satisfactory.

boiling the solution for some time with hydrochloric acid the original hydroxylactone appears as a colourless oil.

The authors have pleasure in acknowledging that much of the expense of this work was defrayed from grants from the Research Funds of the Chemical Society.

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XV.—*Studies in Optical Superposition. Part IV. l-Menthylamine Tartrates and l-Amyl Dimethoxysuccinates.*

By THOMAS STEWART PATTERSON and DOROTHY CHRISTINA PATTERSON (late Carnegie Research Scholar).

THE so-called principle of optical superposition, which is due to van't Hoff, asserts that if in a molecule containing several asymmetric carbon atoms the part of the total rotation due to any one of these be $+\alpha°$, then on replacing that atom by its mirror image the latter should be responsible for $-\alpha°$ of the rotation of the new compound. The validity of this assumption is of some importance because if the assumption be true, the rotation of, for example, *d-sec.*-butyl *dl*-tartrate must be that of the active butyl radicle when in combination with either the *d*- or the *l*-tartaryl radicle, whilst that of *dl-sec.*-butyl *d*-tartrate must be the rotation of the active tartaryl radicle in combination with either the *d*- or the *l-sec.*-butyl group. It would therefore be possible to resolve the rotation of *d-sec.*-butyl *d*-tartrate into two parts, one being the rotation of the butyl radicle and the other that of the tartaryl radicle. By a procedure something like this Walden and Guye sought to establish the truth of van't Hoff's assumption, but as was shown in previous parts of this investigation (T., 1905, **87**, 33; 1906, **89**, 1884; 1907, **91**, 705) their method of proof completely eliminated the influence they wished to study, and it is easy to show that the experimental results which they arrived at would be obtained even if the principle were quite false.* It

* See also Guye and Gautier, *Zeitsch. physikal. Chem.*, 1907, **58**, 659. These authors appear to justify the proof of the principle of optical superposition by what they call the method of partially racemic esters, a method which is entirely fallacious, and they refer also to a second proof of the principle, which consists in determining the rotation of such a substance as *l*-amyl *l*-valerate and comparing

seems strange that van't Hoff, to whom more perhaps than to anyone else we are indebted for the idea that the spatial arrangement of the atoms of a molecule is a very important factor in conditioning its properties, should have been reluctant to admit the probability of the rotations of these superimposed radicles being mutually affected owing to different relative position, in the compound molecule, of the groups composing them. ("Die Lagerung der Atome im Raume," 3te. Auf., 1908, pp. 6, 7, 19, 95.) Maleic acid and fumaric acid differ in melting point and other properties simply because of the different relative arrangement of the atoms of their molecules. The melting point of *d*-tartaric acid (170°) differs from that of *i*-tartaric acid (143°) for just the same reason, but in the latter case two of the carbon atoms are asymmetric, so that optical superposition is directly involved in this difference in melting point. It therefore seems reasonable to suppose that a *d*-tartaryl group, $H-\overset{CO_2H}{\overset{|}{C}}-OH$, would have different rotatory values according as it is in combination with a *d*-tartaryl or an *l*-tartaryl radicle.

In connexion with this matter van't Hoff (*loc. cit.*, p. 97) lays some stress on the fact that in certain cases active derivatives of isomeric radicles show comparatively little difference in rotation, as in the case of propyl and *sec.*-propyl glycerates with specific rotations of $-12{\cdot}9°$ and $-11{\cdot}8°$ respectively, and he expressed the opinion that a compound in which the asymmetry depended on the difference between a propyl and a *sec.*-propyl group, such as propyl *sec.*-propylacetic acid, should show "nur

this with the sum of the rotations of two other esters, one containing the *l*-amyl radicle attached to an acid radicle of approximately the same weight as the valeryl radicle but inactive, *n*-valeryl, for example, and the other containing the active valeryl radicle together with an inactive alkyl radicle such as *iso*amyl. The sum of the rotations of the two latter esters is 5·34, almost identical with that of the first, namely 5·32° ($l=0{\cdot}5$ dcm. in each case), on which account they say that the principle of optical superposition is established. These considerations, they remark, have at the present time all the greater applicability especially when one remembers that substitution remote from the asymmetric atom has only a slight influence on rotation. Now it is of course true that this regularity is observed in many cases, as was pointed out first by P. F. Frankland and MacGregor (T., 1896, **69**, 121), and especially will it be true in the case of amyl alcohol, the rotation of which is comparatively little subject to change in any case. Guye and Gautier's considerations are, however, no proof of the principle of optical superposition, since it is obviously illegitimate to test a general proposition by means of a particular case, where, a priori, the effect sought for is likely to be so small as to fall within the limits of experimental error. The moral to be drawn from this consideration is rather that in testing the principle of optical superposition compounds should be chosen in which a maximum, not a minimum, effect is likely to be found.

unwesentliche Drehung." It has since been shown, however, as a result of his suggestion, that propyl *sec.*-propylcyanoacetic acid has $[\alpha]_D^{20}$ +11·3° in toluene (*p*: 10) (Fischer and Flatau, *Ber.*, 1909, **42**, 2981), and that, although propyl *sec.*-propylacetic acid could not be resolved, *n*-butyl *sec.*-butylacetic acid has $[\alpha]_D^{20}$ +5·73° (Fischer, Holtzapfel, and Gwinner, *Ber.*, 1912, **45**, 247), whilst Pickard and Kenyon in another connexion (T., 1912, **101**, 624) have found for propyl-*sec.*-propylcarbinol $[\alpha]_D^{20}$ +21·25°. The influence of isomerism in these substances appears, therefore, to be considerably greater than van't Hoff had expected.

The problem of optical superposition is difficult to attack directly, so the work of the previous parts of this investigation was planned on what seemed to be the most suitable method, namely, comparison of the rotation constants of compounds obtained by combining with some other active radicle the three forms of a substance capable of existing in a *d*-, an *l*-, and an *i*-variety. The dimenthyl esters of diacetyl-*d*-, *l*-, and *i*-tartaric acids were examined, when it was found that the mean of the rotations of the *d*- and *l*-compounds, instead of being equal to that of the *i*-compound, as van't Hoff's assumption would require, differed from it at 20° in the homogeneous condition by 33·5° (the difference becoming less as the temperature rises) and by 25·5°, 51°, and 52·5° at the same temperature in ethyl alcohol (*p*: 0·455), benzene (*p*: 5), and nitrobenzene (*p*: 5) respectively. These results thus agreed with an observation previously made by Walden in a different connexion, who found that the molecular rotation of di-*l*-amyl *i*-tartrate exceeded that of di-*l*-amyl *dl*-tartrate by 4·06° (*Zeitsch. physikal. Chem.*, 1896, **20**, 377). Unless these differences are due to experimental error they are sufficient to disprove the principle of optical superposition.

More recently some work on this subject has been carried out by Tschugaev and Glebko (*Ber.*, 1907, **46**, 2752) by the same method as was adopted by Patterson, Taylor, and Kaye. These authors found that the *l*-menthylurethane derived from the ethyl ester of *i*-tartaric acid by the action of *l*-menthylcarbimide differs by only 2 per cent. of its rotation from the mean of the rotations of the urethanes derived from the esters of the *d*- and the *l*-acids, whilst in the case of the *D*-*l*-fenchylurethanes the percentage difference is about twice as great. They conclude that their results agree with the demands of the principle of optical superposition, at least as a first approximation. The really important question, however, is whether the differences are greater or less than the experimental error. If they are greater van't Hoff's assumption is disproved, but—and this is a point that has not previously been

put forward, and upon which we wish to lay particular stress—the converse is not necessarily true. It is carefully to be noticed that even if the mean value for the *d*- and the *l*-compounds were identical with the value for the rotation of the *i*-compound, the fact would not necessarily be a proof of the principle of optical superposition. It may, in fact, well be that in a series of compounds containing two or more asymmetric centres the mutual influence of the active groups in the several cases might, when studied by this method, be such as to mask the effect. This will perhaps be rendered most clear by according imaginary values to a set of compounds such as the *l*-amyl esters of *d*-, *l*-, and *i*-tartaric acids, on the assumption that the principle of optical superposition does not hold.

R	(+10°)	R	(+20°)	R	(+13°)
H–C–OH	(+15°)	HO–C–H	(−18°)	H–C–OH	(+14°)
HO–C–H	(+15°)	H–C–OH	(−18°)	H–C–OH	(−16°)
R	(+10°)	R	(+20°)	R	(+17°)
l-Amyl *d*-tartrate. (I.)		*l*-Amyl *l*-tartrate. (II.)		*l*-Amyl *i*-tartrate. (III.)	

In the compound I, let the *l*-amyl radicles contribute each +10° to the rotation, and each of the asymmetric centres of the acid contribute 15°, whereas in the compound II, each *l*-amyl radicle contributes 20° and each *l*-tartaryl radicle −18°. In the compound III it would perhaps be most natural to expect the rotatory power of these different centres to lie more or less intermediate between the values in the compounds I and II. Half the rotation of the compound I gives the rotatory value of the group R H–C–OH when attached to an exactly similar group, whereas half the rotation of the compound II gives the rotatory power of the radicle H–C–OH when combined with a group identical with itself. R

The sum of these would be the rotation of the two groups in combination, assuming that they exert no influence on each other, whereas the rotation of the compound III is the sum of the rotations of these two groups plus any change of rotation due to the influence of optical superposition, and it will probably be clear that in certain cases a positive change in the rotation of the upper group might be masked by a negative change in the rotation of the lower group. Of course, in certain other cases the effect might be an enhancement. It will be clear, however, that the difference upon which we have to depend is merely a subsidiary or secondary

effect. In the imaginary example quoted above the mean of the rotations of I (+50°) and II (+4°) is 27°, whilst the rotation of the compound III is 28°, only one degree more. A slightly different choice of values would make this difference zero. Thus, even if the mutual influence of the different centres were very great indeed and the principle of optical superposition altogether violated, the mean of the rotations of two compounds of the type of I and II might, owing to a compensation of effects, be exactly equal to that of the compound III. It must carefully be noticed, therefore, that a negative result by our method may indicate, but is by no means necessarily a proof of, the correctness of this principle, whereas even a small positive result, provided, of course, it falls outside the limit of experimental error, may in reality indicate a wide departure from it, and is definitely a proof that van't Hoff's assumption is incorrect.

The present paper deals with two sets of three compounds each, similar to those referred to above, namely, the three di-*l*-menthylamine tartrates and the three di-*l*-amyl dimethoxysuccinates. The rotations of the three menthylamine tartrates were examined in methyl-alcoholic solution at a concentration of $c=1{\cdot}311$ and at a temperature in the immediate neighbourhood of 22°, it having been found that a slight change of temperature of one or two degrees made no appreciable difference upon the rotations of the solutions. The numbers obtained were as follows:

l-Menthylamine Tartrates.

Methyl-alcoholic solution, $c=1{\cdot}311$.

	$[M]_D^{22}$.
l-Menthylamine *l*-tartrate	−193·2°
„ *d*-tartrate	−57·9
Mean	−125·5
l-Menthylamine *i*-tartrate	−147·5

The mean of the rotations of the *l*- and *d*-derivatives differs by 22° from the rotation of the corresponding *i*-tartrate, this agreeing roughly with Walden's results for the amyl tartrates, and with Patterson, Taylor, and Kaye's for the di-*l*-menthyl diacetyltartrates.

For our second series of compounds we thought it desirable to use an acid with as high a rotation as possible, and therefore chose dimethoxysuccinic acid, the different forms of which we have combined with *l*-amyl alcohol, and in the future intend to combine with other active alcohol-radicles.

The results obtained were as follows:

Di-l-amyl Esters of the Dimethoxysuccinic Acids.

	$[M]_D$.			
	20°.	60°.	100°.	140°.
l-Acid.....	−225·1°	−212·7°	−199·8°	−186·4°
d-Acid	+240·5	+230·3	+220·1	+209·2
Mean	+7·7	+8·8	+10·15	+11·4
i-Acid.....	+12·2	+11·86	+11·62	+11·46*

* Extrapolated.

It will be noticed that here again at a temperature of 20° the mean value of the rotations of the derivatives of the *d*- and the *l*-acid, namely, +7·7°, differs from the value obtained for the rotation of the derivative of the *i*-acid, +12·2°, by some 5°, which, considering that the rotation of the derivatives of the *d*- and the *l*-acid extend over a range of some 500°, does not seem very much, but which compared with the rotation of *l*-amyl alcohol is not inconsiderable. It is thus merely a question whether this difference is greater or less than the experimental error, and the experimental error could only be determined in this case by repeating the whole investigation. That, however, as we had only a small supply of *l*-amyl alcohol, was impracticable, but attention may be directed to an interesting point which appears to bear upon this question. It will be noticed that as the temperature rises the mean value for the rotations of the derivatives of the *d*- and the *l*-acid gradually increases from +7·7° at 20° to +8·8° at 60°, to 10·15° at 100° and to 11·4° at 140°, whereas the rotation of the derivative of the *i*-acid gradually diminishes with increase of temperature, reaching the values +11·86° at 60°, 11·62° at 100°, and 11·46° at 140°. In other words, that at 140° the mean value of the *d*- and the *l*-derivatives is almost identical with that of the *i*-derivative. Now it must also be noticed, as is rendered most clear by plotting these two series of numbers on a diagram, that this is not a case in which two curves approach a common value asymptotically, but that the graphs would intersect in the immediate neighbourhood of 140°, and then separate again. Now if the principle of optical superposition were true it would surely be expected that these two values should be identical at all temperatures, or that they should differ at different temperatures only to a slight extent and in an irregular manner. The fact that this is not the case seems to us a strong indication, in the first place that these differences are not due to experimental error, and, in the second place, that the mutual effect of the different asymmetric centres varies with change of temperature, so that at 140° there is realised in this series of compounds the state of affairs referred to above (p. 146), where in spite of the assumed falsity of the principle of optical

superposition the various effects balance one another in such a way as to give a result identical with that which should be obtained if this principle were in fact true.

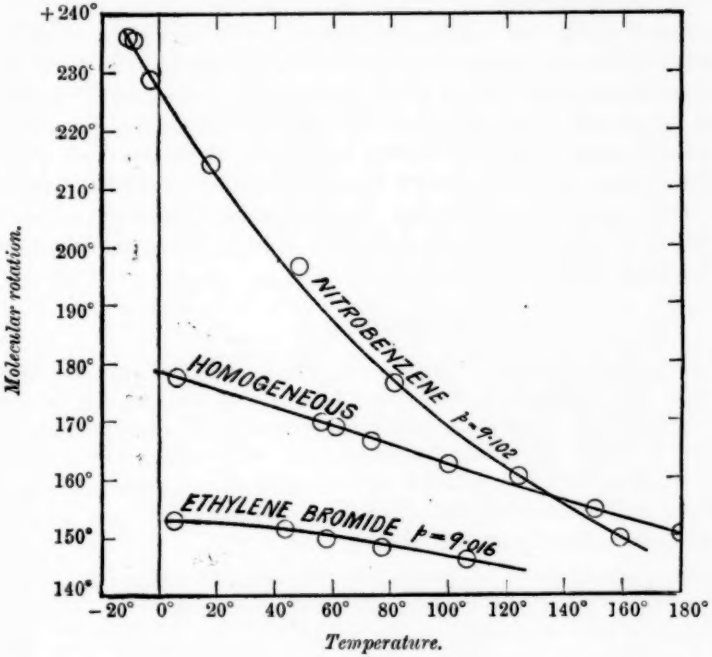
It would therefore seem that all the work theoretically sound which has been carried out or this subject by Walden, by Tschugaev and Glebko, by Patterson, Taylor, and Kaye, and by ourselves is decidedly out of agreement with the requirements of the principle of optical superposition. It ought, however, to be mentioned that our present results also contain a slight element of uncertainty since the *l*-amyl alcohol used in the investigation had α_D^{20} (100 mm.) $-4{\cdot}58°$, whereas the purest obtained by Marckwald (*Ber.*, 1901, **34**, 485) had $[\alpha]_D^{20} -5{\cdot}90°$, which since $D_4^{20} = 0{\cdot}816$ would give for the observed rotation $\alpha_D^{20} -4{\cdot}812°$, $0{\cdot}232°$ higher than ours. Since the impurity contained in the alcohol is an inactive substance it is not likely to affect the results to any great extent. Nevertheless, the objection does exist.

It is of some interest to notice that the density of *l*-amyl *l*-dimethoxysuccinate is greater than that of *l*-amyl *d*-dimethoxysuccinate only by one or two units in the fourth place, whilst the density of *l*-amyl *i*-dimethoxysuccinate is greater at 20° than that of the other two by about four units in the third place. This difference diminishes, however, as the temperature rises, in such a way that in the neighbourhood of 130° the densities of all three would be the same. At higher temperatures, presumably, the density of the *i*-derivative would be less than that of either of the other two.

We wish particularly to direct attention to a slightly improved method for the preparation of alkyloxy-esters. The *d*- and the *l*-dimethoxysuccinic esters used by us were prepared exactly according to the method of Purdie and Irvine (T., 1901, **79**, 957), but during the course of our work it occurred to us that the process might be improved. On the one hand it has been shown by J. W. Walker (T., 1895, **67**, 914) that in the esterification of a hydroxy-acid by the silver salt method a product is obtained having a much higher rotation than the ester which has been prepared from the acid and the alcohol (see also Purdie and Williamson, T., 1896, **69**, 821, *passim*.), and it was shown by Purdie and Lander (T., 1898, **73**, 288) that this is due to the formation of some alkyloxy-derivative. Then, on the other hand, Purdie and Pitkeathly (T., 1899, **75**, 160) state that when tartaric acid is alkylated directly with ethyl iodide and silver oxide a fairly good yield of ethyl diethoxysuccinate is obtained. It would therefore appear that the simplest and quickest way of preparing the alkyloxy-derivative of an ester would be to produce the simple ester from the silver salt

of the acid by the action of alkyl iodide and simultaneously to convert this into the alkyloxy-compound by means of further alkyl iodide and silver oxide. Thus to prepare dimethyl dimethoxysuccinate, silver oxide and methyl iodide are heated in a flask under reflux to the boiling point of the iodide, silver tartrate being then added from time to time in portions of 5 or 6 grams. This method gives practically a quantitative yield. Its special advantage lies in the fact that it is generally much easier and quicker to make the silver salt of an acid than to make the methyl ester. In addition

Rotation of dimethyl d-*dimethoxysuccinate in the homogeneous condition and in solution in nitrobenzene and in ethylene bromide.*



the whole course of the reaction is smoother and simpler than by the method of Purdie and Irvine (see p. 154).

We have also taken the present opportunity to examine the rotation of dimethyl *d*-dimethoxysuccinate over a considerable range of temperature both in the homogeneous condition and in solution in nitrobenzene and in ethylene bromide, two solvents which, on ethyl tartrate at least, exert quite opposite effects.

The results are shown graphically in the diagram. The rotation of the homogeneous ester diminishes with rise of temperature

almost linearly, but we are inclined to think that there is probably a point of inflexion in the neighbourhood of 100°, and that below this temperature the rotation tends towards a maximum, and above it towards a minimum value.

Ethylene bromide diminishes the rotation of the ester, and the appearance of the curve in this solvent would suggest the existence of a maximum rotation in the neighbourhood of zero. Nitrobenzene, on the other hand, at ordinary temperatures raises the rotation of the ester to a very considerable extent. In this solvent the temperature-coefficient is large, and the rotation diminishes very much more rapidly on heating than does that of the homogeneous ester. It is interesting to notice that there is here no point of inflexion apparent, and that the temperature-rotation curve cuts that for the homogeneous ester. The behaviour of these two solvents on the rotation of this ester is thus similar to their influence on the rotation of ethyl tartrate, and suggests that here also a maximum rotation occurs at the ordinary temperature in the solvent producing the lowest rotation; that in the homogeneous ester this maximum moves towards a higher value at a lower temperature; whilst in nitrobenzene a much greater maximum rotation would be found at a still lower temperature (see T., 1913, **103**, 157).

Experimental.

Di-l-*menthylamine* d-*Tartrate*, M = 460.—This salt, which was prepared by adding two molecular proportions of *l*-menthylamine to a concentrated aqueous solution of tartaric acid, was purified by solution in ethyl alcohol and precipitation with ether. On heating, slight traces of liquid appeared on the walls of the containing tube at about 90°, darkening in colour occurred at 190°, and the salt melted fairly sharply at 198°:

0·3988 gave 21·6 c.c. N_2 (moist) at 15° and 752·6 mm. N = 6·29.
$C_{24}H_{42}O_6$ requires N = 6·08 per cent.

0·3448 of this specimen, made up to 26·3 c.c. (c = 1·3111) with ordinary pure methyl alcohol (acetone-free), gave $\alpha_D^{22·6}$ [l = 400 mm.] −0·66°, whence $[\alpha]_D^{22·6}$ −12·585°, and $[M]_D^{22·6}$ −57·89°.

Di-l-*menthylamine* l-*tartrate* was prepared from *l*-tartaric acid, 2·463 grams of which, made up to 26·3 c.c. with water, gave $\alpha_D^{19·5}$ [l = 400 mm.] −5·387°, whence $[\alpha]_D^{19·5}$ −13·4°. A specimen of ordinary laboratory tartaric acid gave, under the same conditions, α_D^{19} [l = 400 mm.] +5·34°. One gram of this acid, mixed with 2·12 grams of *l*-menthylamine and 8 c.c. of water, gave, on keeping overnight, large, flat crystals, readily soluble in methyl or ethyl

alcohol. The specimen used was purified by solution in ethyl alcohol and precipitation by ether. On heating it showed traces of liquid on the walls of the containing tube at about 120°, and melted fairly sharply at 194°:

0·4 gave 20·7 c.c. N_2 (moist) at 19° and 776·3 mm. N = 6·08.
$C_{24}H_{42}O_6$ requires N = 6·08 per cent.

0·2448 of this substance, made up to 26·3 c.c. (c = 1·3111) with ordinary pure methyl alcohol (acetone-free), gave $\alpha_D^{20·7}$ [l = 400 mm.] −2·203°, whence $[\alpha]_D^{20·7}$ 42·005° and $[M]_D^{20·7}$ −193·2°.

Di-l-*menthylamine* i-*Tartrate*.—The *i*-tartaric acid used in this investigation was prepared by the method worked out by Winther (*Zeitsch. physikal. Chem.*, 1906, **56**, 507). On shaking an aqueous solution of the acid with the calculated quantity of *l*-menthylamine the salt separates at once. After two crystallisations from absolute ethyl alcohol it melted at 218°. It was decidedly more readily soluble in methyl alcohol. The specimen used was purified by solution in absolute ethyl alcohol and precipitation by ether:

0·4014 gave 21·5 c.c. N_2 (moist) at 19° and 750·6 mm. N = 6·17.
$C_{24}H_{42}O_6$ requires N = 6·08 per cent.

0·3448 of this salt, made up to 26·3 c.c. (c = 1·3111) with ordinary pure methyl alcohol (acetone-free), gave α_D^{22} [l = 400 mm.] −1·682°, whence $[\alpha]_D^{22}$ −32·07° and $[M]_D^{22}$ −147·5°.

Dimethyl d-*dimethoxysuccinate* was prepared from methyl *d*-tartrate exactly according to Purdie and Irvine (T., 1901, **79**, 957). It boiled at 135°/16 mm., and melted at about 49°.

Rotation of Dimethyl d-*Dimethoxysuccinate*.

t	15°	16°	55·9°	60·5°	73·2°	100°	150°	182°
α_D^t (100 mm.)*	+101·6°	101·35°	93·56°	92·64°	90·26°	85·66°	77·99°	72·81°
d	1·178	1·177	1·136	1·129	1·117	1·088	1·0355	0·998
$[\alpha]_D^t$	86·2°	86·1°	82·4°	82·1°	80·8°	78·7°	75·3°	73·00°
$[M]_D^t$ ...	177·7°	177·4°	169·7°	169·0°	166·4°	162·2°	155·2°	150·3°

Densities determined:

t	65·3°	69·6°	80·6°	99·8°	153°
d	1·1251	1·1204	1·1088	1·0881	1·0328

* The rotations were determined in a brass tube (l = 30·48 at 20°) and were corrected for expansion of the tube on heating and then calculated to a 100 mm. layer of the liquid at the temperature of the experiment.

Dimethyl d-*Dimethoxysuccinate in Ethylene Bromide.*

$p = 9{\cdot}016$.

t	14·9°	43·5°	57·8°	76·7°	106°
α^t_D (100 mm.)*	+13·576°	13·09°	12·74°	12·37°	11·85°
d	2·026	1·971	1·945	1·909	1·852
$[\alpha]^t_D$	74·3°	73·6°	72·7°	71·8°	71·00°
$[M]^t_D$	153·1°	151·6°	149·7°	148·0°	146·2°

Densities determined:

t	15·8°	44·9°	88·5°
d	2·0254	1·9690	1·8851

* In a glass tube.

Dimethyl d-*Dimethoxysuccinate in Nitrobenzene.*

$p = 9{\cdot}102$.

t	−10·6°	−8·8°	−3·2°	+18·4°	48·3°	81°	124·5°	159·5°
$[\alpha]^t_D$ (100 mm.)*	+12·82°	12·78°	12·35°	11·37°	10·07°	8·88°	7·77°	7·02°
d	1·2300	1·2280	1·2225	1·2010	1·1710	1·139	1·096	1·061
$[\alpha]^t_D$	114·5°	114·4°	111·0°	104·0°	94·4°	85·6°	77·9°	72·7°
$[M]^t_D$	235·9°	235·7°	228·7°	214·2°	196·5°	176·4°	160·4°	149·7°

Densities determined:

t	15·6°	43·0°	98·7°	150°
d	1·2041	1·1764	1·1212	1·0707

* Glass tube.

Dimethoxysuccinic acid was prepared exactly according to Purdie and Irvine (T., 1901, **79**, 959). The acid, when recrystallised from water, melted at 153°.

Di-l-amyl d-*Dimethoxysuccinate.*—Ten grams of *d*-dimethoxysuccinic acid were placed in a Claisen flask along with 50 grams of *l*-amyl alcohol, the rotation of which was α^{20}_D [l=100 mm.] −4·58°. Dry hydrogen chloride was then passed into the mixture in the cold for about a day, after which the flask was heated on the water-bath to just below 100°, the passage of dry hydrogen chloride being continued for three or four days. The contents of the flask were then distilled under the ordinary pressure until the temperature rose to 140°, and then for a short time under diminished pressure. When all the amyl alcohol had been removed the *l*-amyl *d*-dimethoxysuccinate was distilled under a pressure of about 9 mm. A small first fraction was collected up to a temperature of about 170°; the main fraction boiled at 175—180°. The crude product had α^{17}_D [l=30·48 mm.] +23·7°. It was then redistilled and boiled at about 170°/3 mm. It was divided into four fractions. The rotations of the last three at 15·9° in a tube of l=30·48 mm. were

II +24·12°, III +24·13°, IV +23·82°. Fractions I and IV were then combined and redistilled, being collected in two portions. Fractions II and III were then similarly treated, and the second fractions from each distillation were combined and finally distilled. The boiling point lay at about 170°/5 mm. The rotation of this substance was then examined over a considerable range of temperature with the following results. A brass tube, gilt inside, was used, allowance being made for the expansion of the brass. The numbers quoted below for observed rotation are those for an actual thickness of 100 mm. at each temperature.

Di-l-*amyl* d-*Dimethoxysuccinate* [M=318].

t	15°	31°	51°	74°	110°	136°	17·2°*
α^t_D (100 mm.)	+78·95°	76·18°	73·25°	69·99°	64·43°	60·44°	78·52°
d	+1·0171	1·0035	0·9870	0·9677	0·9377	0·9157	1·0138
$[\alpha]^t_D$	+77·62°	75·92°	74·22°	72·33°	68·72°	66·01°	77·42°
$[M]^t_D$ ...	+246·8°	241·4°	236·0°	230·0°	218·5°	209·9°	246·3°

Densities determined:

t.....	15·7°	29·0°	45·2°	69·3°	99·6°
d.....	1·0169	1·0057	0·9916	0·9706	0·9460

* After cooling.

Dimethyl *l*-tartrate was prepared from a pure specimen of sodium ammonium *l*-tartrate by the action of pure methyl alcohol and dry hydrogen chloride in the cold. The process was not altogether satisfactory, since the crude ester tended to decompose on distillation. The methyl *l*-tartrate ultimately obtained was induced to solidify by the introduction of a fragment of methyl *d*-tartrate into a few drops on a watch-glass. This brought about crystallisation of this portion, which in turn was used to induce crystallisation of the main portion. The setting up of crystallisation in an active substance by the introduction of a small quantity of the enantiomorph is a somewhat remarkable fact. Although the methyl *l*-tartrate crystallised, it formed in the end only a pasty mass showing no definite melting point.

Dimethyl l-*dimethoxysuccinate* was prepared from some of this methyl *l*-tartrate by treatment with methyl iodide and silver oxide. An ester was obtained boiling at 125—135°/9 mm., the rotation of which was found to be α^{20}_D [l=30·48] −28·72°, and at a higher temperature α^{78}_D [l=30·48] −25·16°, both values being about two degrees lower than the corresponding rotation values of the *d*-ester, this being doubtless due to some racemisation having occurred in the preparation of the methyl *l*-tartrate, which, as explained, had not been satisfactory. The dimethyl *l*-dimethoxysuccinate was therefore crystallised several times from a mixture of ether and

light petroleum until the melting point rose to 52°, and the rotation had reached the same value as was found for the *d*-ester, namely, α_D^{20} [l=30·48 mm.] −28·255°. The ester was thus pure, and was hydrolysed with barium hydroxide as before, giving *l*-dimethoxysuccinic acid * (m. p. 154°), from 10 grams of which *l*-amyl *l*-dimethoxysuccinate was prepared in exactly the same way as was the *l*-amyl *d*-dimethoxysuccinate. The ester boiled at about 160—170°/5 mm., the yield being 14·8 grams. The crude product had $\alpha_D^{18\cdot2}$ [l=25 mm.] −18·16°. This was then redistilled, four fractions being collected, the rotations of which were, in a 25-mm. tube and at 19·5°: I −17·95°, II −18·33°, III −18·05°, IV −17·83°. Fractions II and III were then united, redistilled, and collected in two portions. The boiling point lay about 160°/5 mm. With the second fraction the following observations were made:

Di-l-*amyl* l-*Dimethoxysuccinate* [M=318].

t	17°	33·8°	50°	81·5°	95·5°	137°
α_D^t (100 mm.)	−72·31°	−69·65°	−67·11°	−62·3°	−60·09°	−53·96°
d	1·0155	1·0015	0·988	0·961	0·950	0·915
$[\alpha]_D^t$	−71·21°	−69·55°	−67·94°	−64·83°	−63·25°	−58·98°
$[M]_D^t$ ...	−226·4°	−221·2°	−216·0°	−206·1°	−201·1°	−187·55°

Densities determined:

t	16·3°	31·4°	50·5°	75·1°
d.....	1·0161	1·0036	0·9870	0·9663

Dimethyl i-*dimethoxysuccinate* was prepared as follows: Fifty grams of silver oxide were placed in a flask along with 205 grams of methyl iodide. The flask, fitted to an inverted condenser, was then heated on the water-bath until the methyl iodide boiled. Twenty-four grams of silver *i*-tartrate, which had been prepared by neutralising *i*-tartaric acid with sodium hydroxide and then precipitating with silver nitrate, washing by decantation with water several times, then with alcohol, and finally with ether, and drying on a porous plate overnight. The silver tartrate was added in portions in the course of half-an-hour. The excess of methyl iodide was then distilled off from the water-bath, the residual mass placed in a Soxhlet apparatus, and extracted with ether for about two hours. The crude dimethoxysuccinic ester weighed 13 grams, the yield being thus practically quantitative. The dimethyl *i*-dimethoxysuccinate was recrystallised from ether, in which it is readily soluble. It melts at 68°. The ester crystallises also from benzene in small, diamond-shaped crystals; it is very sparingly

* The whole preparation would doubtless have been much more satisfactory and simple had it been conducted in the same manner as was later that of the *i*-ester.

soluble in light petroleum, but can be recrystallised from it also. Twenty grams of this dimethyl *i*-dimethoxysuccinate were dissolved in about 100 c.c. of water, and hydrolysed by heating on the water-bath for three hours with a little more than the calculated quantity of sodium hydroxide solution. The excess of sodium hydroxide was then titrated exactly with hydrochloric acid, using litmus as an indicator. The solution was filtered and evaporated to dryness. The resulting salt after drying on the water-bath was broken into small pieces, placed in a Soxhlet apparatus, and extracted with ether for some hours. Crusts of small, well-formed crystals soon separated in the flask, and when the extraction was complete the ether was distilled off and the remaining *i*-dimethoxysuccinic acid recrystallised from water, in which, however, it is very readily soluble. It melts at 161°.

Di-l-amyl i-dimethoxysuccinate was prepared from 10 grams of *i*-dimethoxysuccinic acid (which softened a little about 157° and melted fairly sharply at 160—161°) and 50 grams of *l*-amyl alcohol in just the same way as the *d*- and *l*-compounds. The *l*-amyl *i*-dimethoxysuccinate was distilled under a pressure of about 3 mm. After a small first fraction had been collected at 155°, a second main fraction of 14 grams was collected between 153° and 175°, but chiefly at 155°/3 mm. It had α_D^{16} [l=100 mm.] +3·916°. This fraction was then redistilled under 3 mm. pressure, and a small first fraction removed. The second fraction boiled at 155°/3 mm.; it had α_D^{17} [l=100 mm.] 3·913°, practically identical with the previous value.

l-Amyl i-Dimethoxysuccinate [M=318].

t	17°	37·5°	60°	91·6°	20·4°
α_D^t (100 mm.)	+3·913°	3·780°	3·664°	3·487°	3·905°
d	1·0196	1·0017	0·9819	0·9544	1·0167
$[\alpha]_D^t$	+3·84°	3·77°	3·73°	3·65°	3·84°
$[M]_D^t$	+12·21°	12·00°	11·87°	11·62°	12·21°

Densities determined:

t	17·6°	42·35°	70·4°	99·2°
d	1·0193	0·9973	0·9726	0·9479

In conclusion, we have pleasure in acknowledging our indebtedness to the Carnegie Trustees for the Universities of Scotland for a grant which defrayed most of the expense of this investigation.

ORGANIC CHEMISTRY DEPARTMENT,
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XVI.—*The Rate of Saponification of Derivatives of Ethyl Benzoate.*

By Hamilton McCombie and Harold Archibald Scarborough.

The velocity of saponification by alkali hydroxides of the esters of fatty acids with such primary alcohols as ethyl alcohol and methyl alcohol has been studied very fully by many investigators. With few exceptions, however, none of these workers seems to have studied completely substituted methyl and ethyl benzoates. Meyer and Kellas (*Zeitsch. physikal. Chem.*, 1897, **24**, 221), in their historical research on substituted methyl benzoates, tabulate their results as the percentage of ester saponified in a given interval of time. As a consequence their figures depend on only one observation, except in such cases when the same ester has been examined twice. Even in those cases where these authors examined the behaviour of the same ester twice the results are not concordant. Thus in one experiment the ratios of the quantities of methyl *o*-toluate and methyl benzoate saponified in the same time was found to be 0·08, whilst in a second experiment the ratio was 0·33. This lack of concordance is to be found in every case in which a direct comparison is possible, but in some cases the difference might be due to a very small experimental error.

In these circumstances it was thought desirable to examine the velocity of saponification of the methyl and ethyl esters of the substituted benzoic acids in as complete a manner as possible, examining the reaction over a range of 60—70 per cent., except in such exceptional cases as ethyl *o*-toluate, where the rate of saponification is very slow.

Experimental.

The saponifications were carried out in ethyl-alcoholic solution in the manner described by the authors for phenyl benzoate (T., 1914, **105**, 1304).

Liquid esters were distilled twice under diminished pressure; solid esters were recrystallised until a constant melting point was obtained.

The alcohol was dried over lime for four or five days, and was then distilled over lime. This treatment was repeated twice. In preparing the alcoholic potassium hydroxide it was found best rapidly to grind pure potassium hydroxide and add it to the alcohol. Very little heating was thus required, and the amount of carbonate present was found to be very small.

The reaction was followed at 30°±0·05°. The indicator employed

was phenolphthalein. In the reaction-mixture at the commencement there were present 1·25—2 molecular proportions of potassium hydroxide and 1 molecular proportion of the ester.

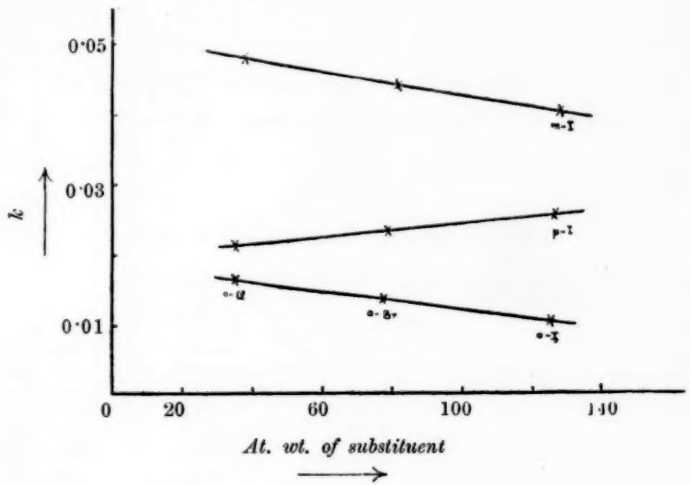
Discussion of the Results.

The reaction is bimolecular, and may be represented by the equation:

$$C_6H_5{\cdot}CO_2{\cdot}C_2H_5 + KOH = C_6H_5{\cdot}CO_2K + C_2H_5{\cdot}OH.$$

A consideration of the results given in tables I—XIII shows that:

(1) Halogen substituents show a marked increase in the velocity of saponification in comparison with the unsubstituted ester.



(2) The influence of the halogen is greatest in the meta-, and least in the ortho-position.

(3) In comparing the effects of the different halogen substituents it is found that chlorine has a greater influence than bromine, and bromine a greater influence than iodine. An exception to this is encountered in the case of the para-substituted derivatives, when this order is found to be reversed. This strange reversal has been found also in the case of the methyl esters, and, further, it was noticed by Meyer and Kellas (*loc. cit.*).

If curves are plotted (see figure) showing the relationship between the atomic weight of the halogen substituent and the velocities of saponification, these are found to be straight lines. Thus it is seen that the values of k for the bromo-substituted

esters are a mean between the values of k for the corresponding chloro- and iodo-substituted esters.

(4) The influence of the methyl group is in the opposite direction to that of the halogens.

TABLE I.

Ethyl Benzoate. B. p. 96·5°/13 mm.

$a = 0{\cdot}5097 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02232$N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k.
4	21·90	0·94	0·0210	0·00538
8	21·04	1·80	0·0402	0·00549
12	20·29	2·55	0·0569	0·00542
17	19·54	3·30	0·0737	0·00528
26	18·09	4·75	0·1060	0·00543
37	16·76	6·08	0·1375	0·00544
43	16·13	6·71	0·1497	0·00545

Mean of 12 determinations..... $k = 0{\cdot}00543$

Amount of ester saponified in 43 hours is 44·9 per cent.

TABLE II.

Ethyl o-*Toluate.*

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415$N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k.
6	21·76	0·37	0·0089	0·00143
12	21·44	0·69	0·0167	0·00138
20	21·05	1·08	0·0261	0·00132
31	20·54	1·59	0·0384	0·00129
44	19·90	2·23	0·0538	0·00133
51	19·60	2·53	0·0611	0·00133
69	18·87	3·26	0·0787	0·00133

Mean of 12 determinations..... $k = 0{\cdot}00134$.

Amount of ester saponified in 69 hours is 23·6 per cent

TABLE III.

Ethyl m-*Toluate.*

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415$N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k.
6–69	21·10–15·01	1·03–7·12	0·0248–0·173	0·00402 – 0·00414

Mean of 12 determinations..... $k = 0{\cdot}00405$.

Table IV.

Ethyl p-*Toluate.*

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
6–69	21·4–16·65	0·73–5·48	0·0176–0·1323	0·00268 – 0·00288

Mean of 12 determinations..... $k = 0{\cdot}00275$.

Table V.

Ethyl o-*Chlorobenzoate.* B. p. 122·5°/15 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5	20·56	1·57	0·0379	0·0158
4·5	19·55	2·58	0·0623	0·0156
6·5	18·53	3·60	0·0870	0·0161
8·5	17·80	4·33	0·1045	0·0156
12	16·60	5·53	0·1335	0·0156
16	15·50	6·63	0·1600	0·0156
20	14·57	7·56	0·1826	0·0157

Mean of 12 determinations..... $k = 0{\cdot}0157$.

Amount of ester saponified in 20 hours is 54·8 per cent.

Table VI.

Ethyl m-*Chlorobenzoate.* B. p. 119°/13 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	18·03–10·37	4·10–11·76	0·0990–0·2840	0·0483 – 0·0492

Mean of 12 determinations..... $k = 0{\cdot}0485$.

Table VII.

Ethyl p-*Chlorobenzoate.* B. p. 118°/14 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	20·05–13·5	2·08–8·63	0·0502–0·2083	0·0204 – 0·0215

Mean of 12 determinations..... $k = 0{\cdot}0208$.

Table VIII.

Ethyl o-*Bromobenzoate.* B. p. 132°/13 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5	20·87	1·26	0·0303	0·0124
4·5	20·05	2·08	0·0502	0·0119
6·5	19·34	2·79	0·0673	0·0117
8·5	18·73	3·40	0·0821	0·0114
12	17·60	4·53	0·1093	0·0117
16	16·56	5·57	0·1345	0·0118
20	15·80	6·33	0·1530	0·0116

Mean of 12 determinations..... $k = 0{\cdot}0118$.

Amount of ester saponified in 20 hours is 45·9 per cent.

Table IX.

Ethyl m-*Bromobenzoate.* B. p. 133°/15 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	18·27–10·64	3·86–11·49	0·0932–0·2775	0·0442 – 0·0455

Mean of 12 determinations..... $k = 0{\cdot}0445$.

Table X.

Ethyl p-*Bromobenzoate.* B. p. 131°/13 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	19·83–13·00	2·30–9·13	0·0555–0·2205	0·0321 – 0·0241

Mean of 12 determinations..... $k = 0{\cdot}0234$.

Table XI.

Ethyl o-*Iodobenzoate.* B. p. 148°/15 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5	21·20	0·93	0·0225	0·00895
4·5	20·54	1·59	0·0384	0·00889
6·5	19·91	2·22	0·0533	0·00886
8·5	19·37	2·76	0·0669	0·00887
12	18·49	3·64	0·0879	0·00800
16	17·61	4·52	0·1091	0·00878
20	16·83	5·30	0·1280	0·00882

Mean of 12 determinations..... $k = 0{\cdot}00884$.

Amount of ester saponified in 20 hours is 38·4 per cent.

TABLE XII.

Ethyl m-*Iodobenzoate.* B. p. 150·5°/15 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	18·55–10·93	3·58–11·2	0·0865–0·2703	0·0403 – 0·0414

Mean of 12 determinations..... $k = 0{\cdot}0408$.

TABLE XIII.

Ethyl p-*Iodobenzoate.* B. p. 153·5°/14 mm.

$a = 0{\cdot}5303 \cdot 10^{-3}$; $b = 0{\cdot}3333 \cdot 10^{-3}$; HCl = 0·02415*N*.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	*k*.
2·5–20	19·63–12·60	2·5–9·53	0·0604–0·2301	0·0251 – 0·0267

Mean of 12 determinations..... $k = 0{\cdot}0258$.

The influences of several other groups were examined roughly, and it was found that the amino-, the methoxy-, and the hydroxy-groups produced marked retardation, whilst the nitro-group had an enormous accelerative influence on the course of the reaction.

The influence of water on the velocity of saponification of ethyl benzoate has also been studied. Attention was drawn to a consideration of this influence by the fact that for ethyl benzoate and potassium hydroxide at 14·4° in aqueous solution $k = 0{\cdot}83$, whilst in absolute ethyl-alcoholic solution $k = 0{\cdot}00543$.

The general method of experiment was similar to that described in the investigation of the influence of substituents. The results are shown in table XIV.

TABLE XIV.

Alcohol. Per cent.	Number of observations.	Range.	*k*.
100	12	44·9	0·00543
96·7	12	86·7	0·02550
93·3	12	79·3	0·04085
90·0	12	85·9	0·05440
83·33	12	76·4	0·0810
73·33	12	83·5	0·108
60·00	12	89·2	0·148

At this stage of the proceedings it seems to the authors impossible to give a satisfactory explanation of this phenomenon, but it is their intention to investigate this reaction in the case of fatty and aromatic esters with a view to ascertain if any generalisation can be reached.

The authors beg to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM. [*Received, Dec.* 1, 1914.]

XVII.—*The Behaviour of Colloids towards Pure and Mixed Liquids. Part I. The Systems Caoutchouc–Benzene–Alcohol and Caoutchouc–Benzene–Acetone.*

By WILLIAM AUGUSTUS CASPARI.

THE precipitation or salting-out of a crystalloid, whether liquid or solid, involves the formation of at least two phases in stable equilibrium, and the whole system can be represented by isothermals which express all possible equilibria obtaining between the three substances concerned. A colloidal substance, if its conditions of precipitation are to be similarly expressed, must, in the first place, pass into and out of solution reversibly. This condition is adequately fulfilled by a considerable number of organic colloids, including caoutchouc. In the second place the colloid must be as little subject to internal change as possible, chemically or physically, when in contact with solvents. Absolute stability in this respect is not to be expected of any organic colloid, but sufficient stability for present purposes is possessed by several. Caoutchouc, for instance, suffers no chemical change by reaction with solvent, but in solution is liable to spontaneous physical decay (deviscification), which affects its solubility markedly, rendering it less easily precipitable. The rate of decay at the ordinary temperature, however, is very slow, especially if material of initially sound quality be taken; in the present experiments such difficulties as proceeded from this cause were few and of minor import. The circumstances attending the precipitation of caoutchouc seemed, therefore, worthy of study from the formal side.

The soluble constituent of natural indiarubber mixes in all proportions with single solvents, for example, benzene; there is no solubility-limit, and no caoutchouc-solvent complexes are formed in heterogeneous equilibrium with liquid, in the absence of precipitants. At high concentrations of caoutchouc the mixtures are jellies; at low concentrations, more or less viscous fluids. On the other hand, caoutchouc is wholly insoluble in precipitants, for example, alcohol or acetone, and their solubility in caoutchouc

is practically negligible. The solvents for caoutchouc are hydrocarbons generally, halogenated hydrocarbons, carbon disulphide, ethers, and certain esters (for example, amyl acetate). The precipitants are alcohols, ketones, nitrogenous bases, and certain esters (for example, ethyl acetate).

Experimental.

The caoutchouc employed was of the same kind as that referred to in a previous paper (T., 1914, **105**, 2143). The solvents were carefully redistilled, and it was, moreover, necessary to apply them in the most anhydrous condition possible. To this end they were stored over sodium (for benzene), calcium (for alcohol), and calcium chloride (for acetone) respectively in bottles connected by glass tubing each to its small burette, and were drawn from these burettes as required.

That a high degree of reversibility obtains in the precipitation and redissolution of caoutchouc was repeatedly demonstrated in the course of the present investigation, and may be gathered from special experiments, such as the following:

To a clear, homogeneous solution of 1·0 gram of caoutchouc in 40·0 c.c. of benzene were added 15·0 c.c. of alcohol. After shaking and keeping for some hours at 20°, the lower layer (containing practically all the caoutchouc) had a volume of 14·8 c.c. Separately, 1·0 gram of caoutchouc was dissolved in 20·0 c.c. of benzene, and precipitated as a clot by shaking with 13·0 c.c. of alcohol. Two days later 20·0 c.c. of benzene were well shaken in, when the liquid again became homogeneous. On adding 2·0 c.c. of alcohol, shaking, and keeping at 20° a lower layer separated out, which again had a volume of 14·8 c.c.

Ethyl Alcohol as Precipitant.—In order to draw up the full diagram of the system caoutchouc–benzene–alcohol, essentially the same methods are in principle available, and were found practicable, as if three liquids were concerned.

(1) Freshly made up solutions of deresinified caoutchouc in benzene, of known concentration, were titrated with alcohol until separation into two phases just set in. Each limiting triad thus obtained represents a point on the binodal curve. The method serves over a short range only, owing to the inordinate viscosity of moderately concentrated caoutchouc solutions. A known weight of substance was dissolved in stoppered bottles with a known volume of benzene, and the precipitant was added in small portions from a burette. The clot produced by each such addition was redissolved by allowing it to swell and shaking vigorously, the bottle being meanwhile hung in a thermostat at 20°. The end-

point was sharp within one drop of precipitant, especially at low concentrations of caoutchouc. Synthetic volume percentages were calculated by taking 0·91 as the specific gravity of the caoutchouc and neglecting volume-changes incurred in mixing, errors due to which would fall within the limits of the general experimental error.

(2) By proceeding in the same way but adding an excess of alcohol, two fluid layers were formed in equilibrium, the lower of which contained the bulk of the caoutchouc, and was viscid or mobile according to circumstances. The composition of each layer yielded a point on the binodal; in addition, tie-lines were thus obtained, indicating the distribution of benzene between caoutchouc and alcohol. Precipitation was carried out at 20° in narrow, graduated cylinders of 50 or 100 c.c. capacity. The lower layer, provided that its content of caoutchouc did not much exceed 10 per cent., settled, on keeping for twenty-four hours, into a homogeneous, but invariably opalescent phase, the volume of which remained constant for weeks. The upper layer, which, except at the highly-curved lowest range of the binodal (see Fig. 2), was quite clear and limpid, was subjected to analysis. Caoutchouc—mostly very low in amount—was determined by evaporation of 25 c.c. The ratio of benzene to precipitant was determined by measuring the refractivity at 20° in a Pulfrich refractometer; experimental curves (which proved very nearly linear) connecting n_D^{20} with composition of benzene–alcohol and benzene–acetone mixtures had previously been drawn up. In calculating the percentage of precipitant in the upper layer, caoutchouc was counted with benzene, to which it approximates in refractivity much more closely than to either of the precipitants. From the relative volumes of the two layers, the composition of the upper layer, and the known total amounts of the three substances, the composition of the lower layer was calculated.

It was observed that the caoutchouc obtained in analysing the upper layers closely resembled the original material in firmness, elasticity, and freedom from tackiness. This, among other indications, afforded some guarantee that the caoutchouc employed was physically homogeneous, and underwent no appreciable alteration during the experiments. If, however, the mixture was allowed to remain for a week or more before or after precipitation, a tendency was observed on the part of the upper layer to contain slightly more caoutchouc than otherwise, the isolated caoutchouc being then somewhat tacky. These would appear to be effects of spontaneous physical degradation.

(2*a*) By method (2) it was possible somewhat to extend the

binodal curve, but the method breaks down when the precipitated clot contains too much caoutchouc to assemble into a homogeneous layer. From this point upwards the binodal could only be pursued approximately, owing to the increasing difficulty of determining the (now very small) proportion of precipitant in the clot. Precipitation was carried out as before; the liquid phase, which was now free from caoutchouc, was analysed refractometrically; the clot was removed, pressed between filter-paper, and transferred to a volumenometer charged with a benzene-precipitant mixture, where its volume was measured.

The results for caoutchouc, benzene, and absolute ethyl alcohol at 20° are given in the subjoined tables. Table I represents figures obtained by method (1), table II by methods (2) and (2*a*).

TABLE I.

Caoutchouc. Grams.	Benzene. c.c.	Alcohol. c.c.	Synthetic Volumes. Caoutchouc.	Benzene.	Alcohol.
0·032	40·0	17·0	0·06	70·1	29·8
0·080	40·0	15·8	0·16	71·6	28·2
0·405	40·0	14·8	0·80	71·8	27·4
2·404	40·0	14·5	4·6	69·9	25·4
4·061	40·0	13·8	7·7	68·7	23·6

TABLE II.

Conjugate Layers, Synthetic Volumes.

Upper.			Lower.		
Caoutchouc.	Benzene.	Alcohol.	Caoutchouc.	Benzene.	Alcohol.
0·65	71·6	27·7	4·7	70·1	25·2
0·14	71·1	28·8	10·6	67·4	22·0
0	64·9	35·1	25·8	60·2	14·0
0	53·6	46·4	37·7	52·8	9·4
0	33·7	66·3	54·0	44·0	3·1
0	31·5	68·5	63·5	36·5	0
0	23·9	76·1	67·4	32·6	0

In the last two experiments the clot doubtless contained some alcohol, but it was not found possible to determine it with any certainty.

Effect of Temperature.—As the temperature rises, the proportion of alcohol in mixtures which will just dissolve caoutchouc rises considerably, or, in other words, caoutchouc becomes less easily precipitable. The following limiting values were found:

TABLE III.

Temperature 40°.

Caoutchouc. Grams.	Benzene. c.c.	Alcohol. c.c.	Synthetic Volumes. Caoutchouc.	Benzene.	Alcohol.
0·2	40·0	18·8	0·37	67·8	31·8
1·0	40·0	18·1	1·8	67·5	30·7
2·0	40·0	17·4	3·7	67·1	29·2

Temperature 60°.

0·2	40·0	21·6	0·35	64·7	35·0
1·0	40·0	23·3	1·7	62·1	36·2
2·0	40·0	24·4	3·3	60·0	36·7

It will be observed that at 60°, for a given volume of solvent, more precipitant is required for a greater amount of caoutchouc than for a less. This indicates that at that temperature the binodal curve soon departs from parallelism with the binodal for 20°, and assumes a strong inward curvature; but it may also be partly caused by the deviscification of caoutchouc, which is much favoured by higher temperatures.

Effect of Moisture.—The precipitation of caoutchouc is brought about by a decidedly smaller volume of precipitant when the latter contains water; moisture, in fact, has the opposite action to increase of temperature. The following limits were found with alcohols containing 5 per cent. and 8 per cent. of water:

TABLE IV.

Alcohol 95 *per cent.*

Caoutchouc. Grams.	Benzene. c.c.	Alcohol (aqueous). c.c.	Synthetic Volumes. Caoutchouc.	Benzene.	Alcohol (aqueous).
0·206	40·0	11·0	0·44	78·0	21·5
0·81	40·0	10·8	1·72	77·3	20·9
2·01	40·0	10·2	4·2	76·4	19·4
3·22	40·0	9·8	6·6	75·0	18·4

Alcohol 92 *per cent.*

0·80	40·0	9·6	1·74	79·2	19·0
2·01	40·0	8·8	4·3	78·4	17·3
3·20	40·0	8·1	6·8	77·5	15·7

Alcohol having a moisture content of more than 8 per cent. caused a separation of water in fine globules, and the system, which now consisted of three possible phases, was not further pursued; nor was a determination (in the two-phase region) of the partition of dissolved water attempted. The results, when compared with

those in table I, illustrate sufficiently the powerful effect of moisture.

Acetone as Precipitant.—The solubility-limits for caoutchouc, benzene, and acetone were determined by method (1) in the same way as with alcohol. Method (2*a*) was also practicable. In that region of the binodal, however, where the lower layer is a fairly dilute solution of caoutchouc, the precipitate showed a tendency to assume a flocculent form. A homogeneous lower layer, such as forms readily with alcohol as precipitant, was not easily obtained. Furthermore, when the lower layer was so dilute as to be homogeneously fluid, the results obtained on analysing the conjugate layers proved somewhat erratic, which may partly be due to the circumstance that spontaneous deviscification in benzene–acetone solutions, as was repeatedly observed, takes place more rapidly than in benzene–alcohol or benzene solutions. Results by method (2) were therefore discarded. The course of the binodal curve at 20° is indicated by the following data:

TABLE V.

Caoutchouc. Grams.	Benzene. c.c.	Acetone. c.c.	Synthetic Volumes. Caoutchouc.	Benzene.	Acetone.
0·11	20·0	15·7	0·31	55·8	43·9
0·80	20·0	15·0	2·45	55·7	41·8
1·86	20·0	14·7	5·56	54·5	40·0

TABLE VI.

Conjugate Layers, Synthetic Volumes.

Upper. Caoutchouc.	Benzene.	Acetone.	Lower. Caoutchouc.	Benzene.	Acetone.
0·21	55·6	44·2	8·95	52·8	38·2
0	48·9	51·1	30·6	45·8	23·6
0	38·9	61·1	48·8	39·5	10·7
0	28·6	71·4	63·6	33·0	3·4

At higher temperatures considerably more acetone is required for precipitation, as is seen from the following limits:

TABLE VII.

Caoutchouc. Gram.	Benzene c.c.	Acetone. c.c.	Synthetic Volumes. Caoutchouc.	Benzene.	Acetone.
Temperature 40°.					
0·10	20·0	19·6	0·27	50·4	49·4
0·98	20·0	17·6	2·79	51·7	45·5
Temperature 60°.					
0·10	20·0	23·0	0·25	45·4	54·3
1·01	20·0	26·4	2·33	42·1	55·6

To the results at 60° the same remarks apply as to those with alcohol (table III).

Moisture again has the opposite, that is, a facilitating, effect on precipitation. A milky liquid containing separated water was formed with as little as 1 per cent. of water in the precipitant. Disregarding this, it was found that 0·5 and 5·0 per cent. solutions of caoutchouc in benzene were precipitated respectively by 55 and 58 volumes per cent. when the acetone contained 2 per cent. of water, whereas of anhydrous acetone 78 and 74 volumes would be required respectively; hence the precipitating effect of water is

FIG. 1.

very considerable. Aqueous acetone brings down the caoutchouc in discrete, flocculent aggregates.

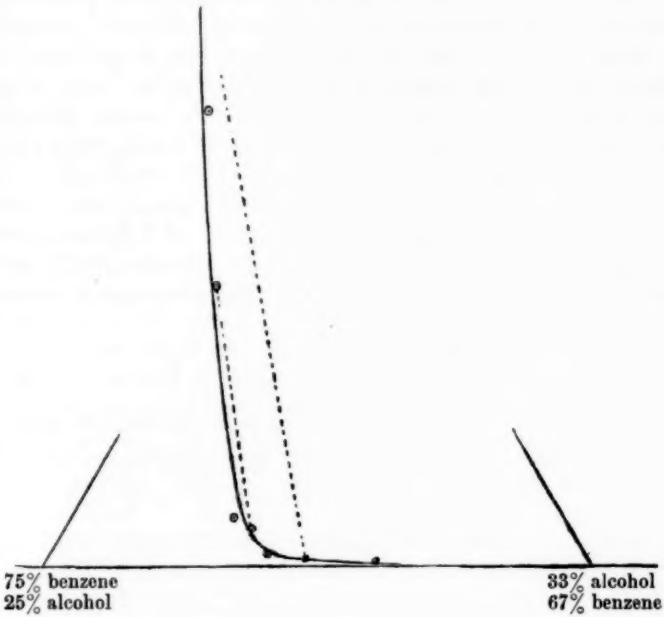
Discussion of the Results.

The isothermal diagrams at 20°, plotted in trilinear co-ordinates, are given for alcohol and acetone in Fig. 1. Conjugate layers are indicated by dotted lines. It will be seen that the binodal curves do not sweep towards A, but appear to cut AB somewhat abruptly; they really meet it, however, at a much gentler angle, as is seen from Fig. 2, which represents a portion of the caoutchouc–benzene–alcohol diagram ten times magnified.

In mixtures containing 43 volumes or more of absolute alcohol

to 100 of benzene, caoutchouc is at 20° practically a completely insoluble substance. The same applies to mixtures containing 80 volumes or more of anhydrous acetone to 100 of benzene. At this end of the binodal, caoutchouc behaves towards mixed solvents like a solid, for example, like sodium chloride towards water–alcohol. Higher temperatures shift the binodal inwards. Mixtures of binodal composition, especially those containing 1—5 per cent. of caoutchouc, show a sensitive and perfectly reversible change from clear to cloudy at the critical temperature. In the presence of moisture the binodal is shifted outwards. Hence in practice the

FIG. 2.



completeness or economy of a caoutchouc precipitation would be favoured by the presence of water and by low temperatures. The nearly vertical impact of the binodal on the benzene-precipitant axis, together with the general slope of the tie-lines, express the fact that when precipitant is added to a solution of a sound caoutchouc, a very small excess in general serves to precipitate the whole of the dissolved substance. From this it follows that such a caoutchouc, even though in reality it may not be a truly homogeneous substance, cannot be separated into components by fractional precipitation.

The upper end of the binodal is not so clearly defined, and it is

uncertain whether the binodal cuts *BC* or continues to *C*. If the former were true there would be a limiting concentration of benzene in a precipitated clot, below which the clot would be wholly free from precipitant. This does not seem probable; but it is evident that the amount of precipitant brought down when the clot is rich in caoutchouc (for example, upwards of 70 per cent.) is extremely small.

The course of precipitation of a given benzene solution of caoutchouc will readily be followed from Fig. 1 by the aid of such lines as *PA* and *QA*. Starting from moderately concentrated solutions (for example, $P=200$ grams per litre), complete precipitation will take place at the binodal, the substance precipitating as a clot and the supernatant liquid being free from caoutchouc. With weak solutions (for example, $Q=50$ grams per litre) there will be at the binodal a separation into fluid layers, both of which are dilute solutions of caoutchouc; but a slight further addition of precipitant, so small that the production of fluid layers requires some care in practice, will convert these into a clot and a caoutchouc-free liquid. Further addition of precipitant extracts more and more benzene from the clot. Formation of fluid layers being disregarded, the quantitative relations are given roughly by the following equation for the binodal of caoutchouc–benzene–alcohol at 20°:

$$\left(\frac{100\,C}{B}\right)^{0{\cdot}24} \times \left(\frac{100\,A}{B}\right) = 60,$$

where A, B, and C are synthetic volumes of alcohol, benzene, and caoutchouc respectively. The equation is valid only for caoutchouc concentrations exceeding 2 per cent. in the original benzene solution.

In reality, however, the binodal is probably no very simple curve. If we consider theoretically the ideal case of a homogeneous colloidal substance which can form isothermally, according to concentration, either a gel or a sol with its solvent, passes sharply from the one to the other, and behaves reversibly throughout, we can suppose more than one possible type of the substance-solvent-precipitant diagram, but in all types there will be a decided inflexion in the binodal at a point corresponding with the sol–gel limit. Caoutchouc approximates somewhat to such a colloid; but, apart from the experimental difficulties, the imperfect discontinuity between caoutchouc–benzene sol and caoutchouc–benzene gel opposes an obstacle to the differentiation of the binodal curve. Nevertheless, there are indications from the experimental results that discontinuities exist near *D*, Fig. 1 (alcohol), and *D′* (acetone). These points represent lower layers in equilibrium with those upper

layers which are just beginning to be free from dissolved caoutchouc. They would correspond with a point *E* representing the concentration of caoutchouc in benzene at the sol–gel transition.

The point *E* would stand, assuming *EDA* to be nearly rectilinear, at approximately 1 volume of caoutchouc to 6 of benzene. Some confirmation of its reality, and that of *D* and *D'*, is afforded by the fact that the present specimen of caoutchouc appeared to absorb about 6 volumes of benzene in swelling before passing into solution. An accurate determination of this datum would be difficult if feasible, but some experiments were made by pouring excess of benzene over known weights of the caoutchouc in measuring-cylinders, and noting the boundary of the gelatinous lower layer, which, after twelve hours, remained stationary for some time before being effaced by diffusion. The results ranged from 6·0 to 6·6 volumes of solvent to 1 of caoutchouc as composing the swollen layer. The experiments of Posnjak (*Koll. Chem. Beihefte*, 1912, **3**, 417), although made with another kind of caoutchouc, yield by extrapolation a ratio of about 1 to 7.

According to this view of the behaviour of caoutchouc, the alcohol diagram (Fig. 1) contains only a small region, *DFG*, of a normal three-liquid system. This region would be bounded by its uttermost tie-line *DG*, and would have a plait-point *F* somewhere on the binodal. The region *CDGA* is one of caoutchouc-free liquids in equilibrium with gels, the relations between the two being expressed somewhat clumsily by the tie-lines. Properly speaking, this is a region of the adsorption of benzene (and no doubt of a little precipitant) by caoutchouc out of solutions of benzene in precipitant, for which the triangular diagram is not the most suitable mode of representation.

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[*Received, Jan. 18th*, 1915.]

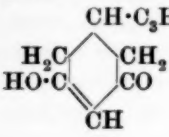
XVIII.—*Hydroaromatic Ketones. Part III.* 1-iso-*Propyl*cyclo*hexan*-3-*one*.

By ARTHUR WILLIAM CROSSLEY and WALTER RYLEY PRATT.

THE preparation of *iso*propyl*cyclo*hexanone was undertaken with the object of preparing from it, by the action of Grignard's reagent, etc., derivatives of the meta-terpene series. As the present authors are unable to continue joint work on the subject,

it is considered desirable to place on record a description of the experiments as far as at present completed, the continuation of the work being reserved for a future communication.

The method of preparation was similar to that used in the case of 1:1:2-trimethyl*cyclo*hexan-3-one (T., 1911, **99**, 1102). When *iso*propyldihydroresorcin (I) (T., 1902, **81**, 675) is treated with phosphorus trichloride it is converted into 5-chloro-1-*iso*propyl-*cyclo*hexen-3-one (II), the constitution of which substance was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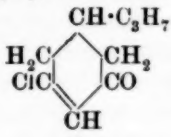
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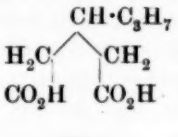
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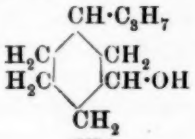
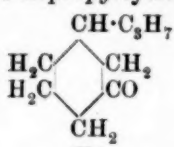

(IV.)

proved by oxidation, as in other similar cases (T., 1903, **83**, 118; 1911, **99**, 1107), when *β-iso*propylglutaric acid (III) was obtained.

On reduction with sodium in moist ethereal solution the chloroketone yields 1-iso*propyl*cyclo*hexan-3-ol* (IV), which should exist in *cis-trans*-forms, and although only one form has been actually isolated, it would appear evident from the following considerations that both forms are really produced. When the crude alcohol is treated with *o*-nitrobenzoyl chloride, it gives in quantitative amount a nitrobenzoyl derivative, which is not homogenous, but consists of 80 per cent. of a solid melting at 48—49°, most probably corresponding with the *trans*-form of the alcohol, and about 20 per cent. of a liquid, which would be for the most part the derivative of the *cis*-form of the alcohol with some of the *trans*-form dissolved in it.

When oxidised with sulphuric acid and potassium dichromate the alcohol is converted into 1-iso*propyl*cyclo*hexan-3-one* (V), which is


(V.)

more susceptible to the action of potassium permanganate than other corresponding ketones of this series that have been examined (compare T., 1907, **91**, 82; 1911, **99**, 1111); for example, dimethyl-*cyclo*hexanone gives *ββ*-dimethyladipic acid in very good yield, whereas *iso*propyl*cyclo*hexanone is degraded to acetone, acetic acid, probably also *iso*butyric acid, and only small quantities of *β-iso*propyladipic acid.

The identification of this acid was rendered easy through the great kindness of Monsieur G. Blanc, who took the trouble to

prepare a specimen of synthetic β-*iso*propyladipic acid for comparison. The authors take this opportunity of expressing their most appreciative thanks to Monsieur Blanc.

Experimental.

The preparation of *iso*propyldihydroresorcin (T., 1902, **81**, 677) has been so modified as to require re-description. Twenty-three grams of sodium (one atom) were dissolved in 275 c.c. of absolute alcohol, 170 grams of ethyl malonate (slight excess over 1 molecule) and 112 grams of *iso*butylideneacetone (1 molecule) added, and the whole heated on the water-bath for two hours. The resulting yellow semi-solid was dissolved in water, evaporated to remove alcohol, the residual alkaline liquid diluted to 2 litres, 90 grams of potassium hydroxide added (solution contained about 10 per cent. of alkali hydroxide), and the whole heated to boiling for fifteen minutes. The liquid was then cautiously acidified with dilute sulphuric acid and boiled until no more carbon dioxide was evolved, when a yellow oil separated, which on cooling solidified, and crystals of *iso*propyldihydroresorcin were deposited. The solidified oil was extracted with water as previously described (T., 1911, **99**, 1105), when, in all, 124 grams of *iso*propyldihydroresorcin were obtained, corresponding with 70 per cent. of the theoretical amount, whereas by the previously described method not more than 50 per cent. was isolated.

The *anilide* of *iso*propyldihydroresorcin was obtained in practically theoretical amount by heating the dihydroresorcin with freshly distilled aniline in benzene solution. It crystallises readily from aqueous alcohol in small, colourless needles, and melts at 175°:

0·1728 gave 8·8 c.c. N_2 (moist) at 16° and 754 mm. N = 5·88.
$C_{15}H_{19}ON$ requires N = 6·11 per cent.

Action of Phosphorus Trichloride on iso*Propyldihydroresorcin.*

Sixty grams (3 mols.) of *iso*propyldihydroresorcin (dried in a vacuum) were heated with 27 grams (1½ mols.) of phosphorus trichloride and 120 c.c. of dry chloroform on a water-bath for three hours, and worked up as previously described (T., 1903, **83**, 117). A determination of chlorine in the resulting liquid (42·5 grams) gave the following result:

0·2195 gave 0·1840 AgCl. Cl = 20·73.
$C_9H_{13}OCl$ requires Cl = 20·57 per cent.

5-*Chloro*-1-iso*propyl*-Δ^4-cyclo*hexen*-3-*one* is a colourless, refractive liquid, boiling at 137°/31 mm., and possessing a very pungent

odour. It is unstable in the presence of moisture, depositing crystals of the hydrochloride of *iso*propyldihydroresorcin (compare T., 1903, **83**, 118).

The *semicarbazone*, prepared in the usual manner, crystallises from alcohol in small, white plates, melting and decomposing at 193°:

0·1148 gave 18·2 c.c. N_2 (moist) at 10° and 748 mm. N = 18·67.

$C_{10}H_{16}ON_3Cl$ requires N = 18·30 per cent.

Oxidation of Chloroisopropylcyclohexenone.—Five grams of the chloro-ketone were suspended in 100 c.c. of water and treated with a 4 per cent. solution of potassium permanganate, until the latter was no longer decolorised, and then worked up in the usual way, when 0·9 gram of solid was obtained, which after crystallisation from water melted at 100° and gave an anilic acid melting at 121—122°. These data prove it to be identical with *iso*propylglutaric acid described by Howles, Thorpe, and Udall (T., 1900, **77**, 942). Both this acid and a specimen of *iso*propylglutaric acid made by oxidising *iso*propyldihydroresorcin (compare T., 1902, **81**, 680) were found to have a somewhat higher melting point, namely, 102—102·5°, after crystallisation from a mixture of chloroform and light petroleum (b. p. 40—60°).

Reduction of Chloroisopropylcyclohexenone.—Quantities of 20 grams of the chloro-ketone were treated with sodium in moist ethereal solution exactly as previously described (T., 1911, **99**, 1108), and the resulting liquid was analysed:

0·1895 gave 0·5291 CO_2 and 0·2113 H_2O. C = 76·14; H = 12·39.

$C_9H_{18}O$ requires C = 76·05; H = 12·67 per cent.

1-iso*Propylcyclohexan*-3-*ol*, the yield of which is 62—64 per cent. of the theoretical amount, is a colourless, viscid, refractive liquid, boiling at 114°/28 mm., showing no signs of solidifying when cooled to −22°, and possessing a peculiar, penetrating odour. It gives with sulphuric acid, either alone or in alcoholic or acetic anhydride solution, an orange-brown colour.

The *benzoyl* derivative, prepared in the usual manner, is an almost colourless liquid, boiling at 210°/39 mm.:

0·1884 gave 0·5400 CO_2 and 0·1520 H_2O. C = 78·17; H = 8·96.

$C_{16}H_{22}O_2$ requires C = 78·05; H = 8·97 per cent.

The *o-nitrobenzoyl* derivative can be prepared in the usual way, but is best prepared by allowing molecular proportions of *o*-nitrobenzoyl chloride and the alcohol to react in pyridine solution. The whole was poured into dilute hydrochloric acid, extracted with ether, washed with potassium hydroxide solution, then water, dried over calcium chloride, and the ether distilled. In this way

10 grams of the alcohol gave 20·2 grams of the nitrobenzoyl derivative which, after spreading on porous plate, gave 16 grams of solid. On crystallisation from alcohol it was obtained in transparent prisms, melting at 48—49°:

0·3802 gave 16·8 c.c. N_2 (moist) at 20° and 759 mm. N = 5·04.
$C_{16}H_{21}O_4N$ requires N = 4·81 per cent.

The alcohol obtained by hydrolysing this substance showed no signs of solidifying when cooled to −22°, and was in all properties indistinguishable from the alcohol prepared by reduction of chloro-*iso*propyl*cyclo*hexenone.

Oxidation of iso*Propyl*cyclo*hexanol.*—Five grams of the alcohol were suspended in 100 c.c. of water, a 4 per cent. solution of potassium hydroxide gradually added, and the whole continuously shaken on a shaking machine. Oxidation took place slowly, requiring fifty hours for completion. The product, worked up in the usual way, gave 3·8 grams of a syrupy, viscid liquid, from which 1·2 grams of solid were obtained on standing. The solid was first treated with chloroform, when a small portion was found to be insoluble. It gave the fluorescein reaction, and melted at 184—185°, nor was this melting point lowered on admixture with pure succinic acid.

The chloroform mother liquor was evaporated, and the residue repeatedly crystallised from water, when it melted at 83—84°, and gave the following figures on analysis, agreeing with those required for an *iso*propyladipic acid (Found, C = 57·10; H = 8·78. $C_9H_{16}O_4$ requires C = 57·44; H = 8·51 per cent.).

The identity of this substance with *β-iso*propyladipic acid was proved by determining the melting point of a mixture of it with a specimen of the synthetic acid kindly sent to the authors by Monsieur G. Blanc.

There was evidence that the liquid portion of the oxidation product contained a ketonic acid, which, however, has not been identified.

Preparation of 1-iso*Propyl*cyclo*hexan*-3-*one.*

This ketone was obtained, using exactly the same conditions as for the preparation of 1:1:2-trimethyl*cyclo*hexan-3-one (T., 1911, **99**, 1110), and gave the following figures on analysis:

0·1959 gave 0·5530 CO_2 and 0·2000 H_2O. C = 76·98; H = 11·34.
$C_9H_{16}O$ requires C = 77·14; H = 11·43 per cent.

iso*Propyl*cyclo*hexanone* is a colourless liquid possessing a pungent, camphoraceous odour, and boiling at 208° or 119°/62 mm. The yield is practically quantitative.

The *semicarbazone* is sparingly soluble in acetone, chloroform, or benzene, and crystallises from alcohol in small, white, glistening plates, melting at 186—187°:

0·1158 gave 21·2 c.c. N_2 (moist) at 17° and 758 mm. N = 21·2.

$C_{10}H_{19}ON_3$ requires N = 21·3 per cent.

The *oxime* is a colourless, viscid liquid, boiling at 155°/37 mm.:

0·2032 gave 15·4 c.c. N_2 (moist) at 20° and 763 mm. N = 8·69.

$C_9H_{17}ON$ requires N = 9·03 per cent.

The *benzoyl* derivative of the oxime is readily soluble in the usual organic solvents, but can be crystallised from alcohol in transparent prisms, melting at 91—92°:

0·2865 gave 13·1 c.c. N_2 (moist) at 8° and 756 mm. N = 5·49.

$C_{16}H_{21}O_2N$ requires N = 5·40 per cent.

Oxidation of iso*Propyl*cyclo*hexanone*.—The ketone is very slowly attacked by potassium permanganate, 10 grams requiring one hundred and fifty hours. The resulting liquid was distilled in a current of steam, and the first portion of the distillate treated with *p*-bromophenylhydrazine, when a crystalline substance melting at 91—92° was obtained, which proved to be the *p*-bromophenylhydrazone of acetone.

The residual liquid was evaporated to a small bulk, acidified with sulphuric acid, and again distilled in steam, when the distillate was proved to contain acetic acid.

The residue from this second distillation was worked up in the usual way, and yielded *β-iso*propyladipic acid melting at 83—84°.

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[*Received, Jan. 21st*, 1915.]

XIX.—iso*Quinoline Derivatives. Part VIII. The Constitution of the Reduction Products of Papaverine* (continued). *The Constitution of Pavine.*

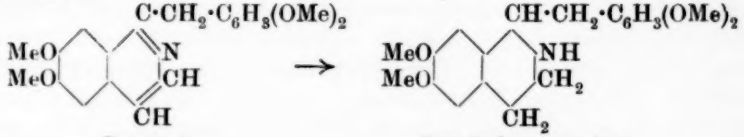
By FRANK LEE PYMAN.

PAPAVERINE, $C_{20}H_{21}O_4N$, yields two products on reduction, an amorphous base, tetrahydropapaverine, $C_{20}H_{25}O_4N$, which forms crystalline salts and derivatives, and a crystalline base, dihydropapaverine, $C_{20}H_{23}O_4N$, which has been designated pavine (Goldschmiedt, *Monatsh.*, 1886, **7**, 485; 1898, **19**, 324; Pyman, T., 1909, **95**, 1610). Similarly, the reduction of *N*-methylpapaverinium salts leads to *N*-methyltetrahydropapaverine

(laudanosine) and *N*-methylpavine (Pictet and Athanasescu, *Ber.*, 1900, **33**, 2346; Pyman and Reynolds, T., 1910, **97**, 1320). Tetrahydropapaverine and pavine are secondary bases, and yield on methylation laudanosine and *N*-methylpavine respectively. The relations between the alkaloids are therefore as follows:

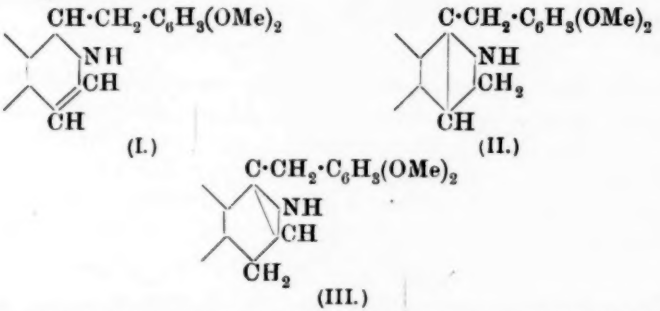
Papaverine, $C_{20}H_{21}O_4N$	→	Tetrahydropapaverine, $C_{20}H_{25}O_4N$	and	Pavine, $C_{20}H_{23}O_4N$
↓		↓		↓
N-Methylpapaverinium salts	→	Laudanosine, $C_{21}H_{27}O_4N$	and	*N*-Methylpavine, $C_{21}H_{25}O_4N$.

The formation of tetrahydropapaverine from papaverine (and of laudanosine from *N*-methylpapaverinium salts) is due to the conversion of the *iso*quinoline into a tetrahydro*iso*quinoline nucleus:



Papaverine. Tetrahydropapaverine.

The formation of pavine by the reduction of papaverine, however, has not been hitherto explained. It involves the addition of two atoms of hydrogen to the papaverine molecule, and one of these certainly occupies a position on the nitrogen atom in the 2-position, since pavine is a secondary base. The second atom of hydrogen must be added at either the 1-, 3-, or 4-position, when pavine would be represented by one of the three corresponding formulæ given below:



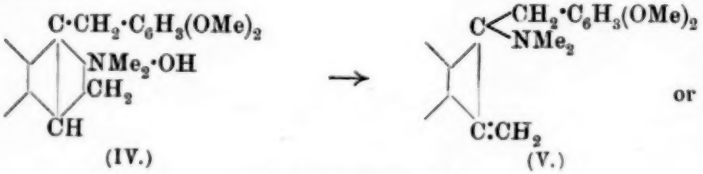
Any one of these formulæ is capable of representing the formation of pavine by the reduction of papaverine, as also the formation of *N*-methylpavine by the oxidation of laudanosine, and each contains one or more asymmetric carbon atoms.* The first formula,

* Pope and Peachey (T., 1898, **73**, 893) have shown that pavine can be resolved into its optically active components (compare also Pope and Gibson, T., 1910, **97**, 2207, 2211).

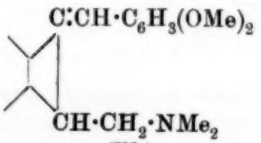
however, represents pavine as a 1:2-dihydropapaverine, and is therefore inapplicable, for 1:2-dihydro*iso*quinolines are readily susceptible of oxidation and reduction (Freund and Beck, *Ber.*, 1909, **42**, 1762), whilst pavine is very stable towards oxidising and reducing agents. A decision between the second and third formulæ has been rendered possible by a study of the degradation of pavine by Hofmann's method, and subsequent oxidation of the product.

In the degradation of a quaternary ammonium hydroxide by Hofmann's method, the hydroxy-group originally attached to the nitrogen atom wanders to a neighbouring carbon atom, and is then eliminated as water with a hydrogen atom from an adjacent carbon atom, yielding an unsaturated substance, termed a methine.

N-Methylpavine methohydroxide, $C_{22}H_{28}O_4N{\cdot}OH$, was converted by the action of boiling concentrated aqueous potassium hydroxide into the *methine*, $C_{22}H_{27}O_4N$, in a yield amounting to 80—90 per cent. of the theoretical. This substance was then oxidised by cold aqueous potassium permanganate, when a *dicarboxylic acid*, $C_{22}H_{27}O_8N$, was obtained in good yield. The formation of this acid is clearly due to the oxidation of an unsaturated grouping, ·CH:CH·. Further, since the acid contains the same number of carbon atoms as the methine, the molecule does not depend for its coherence on the ·CH:CH· group. These facts eliminate the formula (II) for the representation of pavine, for *N*-methylpavine methohydroxide would then have the formula (IV), and yield one of the two methines, (V) and (VI). Neither of these, however, is a possible formula for *N*-methylpavinemethine, since neither can yield a dibasic acid, $C_{22}H_{27}O_8N$, on oxidation, but must become degraded to substances containing a smaller number of carbon atoms:

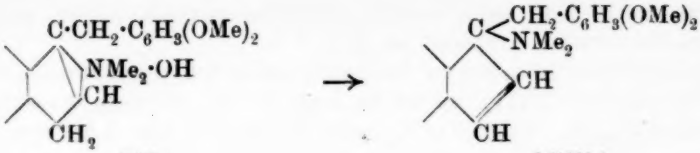


(IV.) (V.)

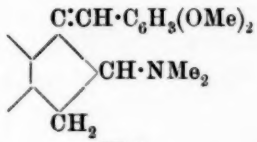


(VI.)

The formula (III) for pavine leads to the formula (VII) for *N*-methylpavine methohydroxide, from which two possible methines, (VIII) and (IX), are derivable by Hofmann's reaction:

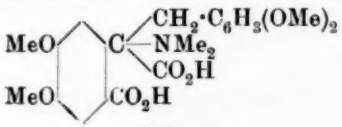


(VII.) (VIII.)



(IX.)

Of these, the latter is impossible, since it would be degraded on oxidation to substances containing a smaller number of carbon atoms. The representation of the methine by formula (VIII), however, readily explains the formation by oxidation of a dicarboxylic acid, $C_{22}H_{27}O_8N$, which would have the formula (X):



(X.)

The evidence afforded by the oxidation of the methine therefore points to the formula (III) for pavine and (VIII) for pavine-methine. It is supported by the behaviour of the methine methiodide towards water and methyl alcohol. When the methine methiodide is boiled with water, it is converted into trimethylamine hydriodide and a neutral *substance*, $C_{20}H_{22}O_5$:

$$C_{23}H_{30}O_4NI + H_2O = C_{20}H_{22}O_5 + N(CH_3)_3,HI.$$

The neutral substance contains, besides four methoxyl groups, one hydroxyl group, which can be replaced by chlorine by means of acetyl chloride, yielding a *compound*, $C_{20}H_{21}O_4Cl$.

Similarly, the methine methiodide is converted by boiling methyl alcohol almost quantitatively into trimethylamine hydriodide, and a neutral *substance*, $C_{21}H_{24}O_5$, which contains five methoxyl groups:

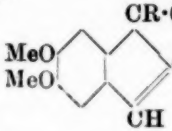
$$C_{23}H_{30}O_4NI + CH_3OH = C_{21}H_{24}O_5 + NMe_3,HI.$$

The grouping $\cdot NMe_3I$ is thus readily replaced by hydroxyl or methoxyl groups. The attachment of the nitrogen atom to the adjacent carbon atom is therefore weak, and this indicates that the carbon atom in question is attached to a negative group, which must here be a benzene nucleus (compare the work of Emde on carbon–nitrogen linkings).

These facts are in good accord with the representation of pavine-

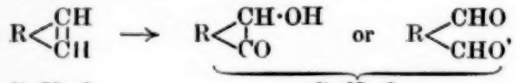
methine methiodide as a benzyltrimethylammonium iodide, and confirm the formula proposed for it.

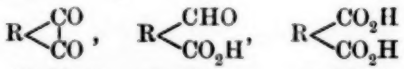
Pavinemethine is therefore 1-*dimethylamino*-1-*homoveratryl*-5 : 6-*dimethoxyindene* (VIII), whilst its degradation products, the substances $C_{20}H_{22}O_5$, $C_{20}H_{21}O_4Cl$, and $C_{21}H_{24}O_5$, are 1-*hydroxy*-, 1-*chloro*-, and 1-*methoxy*-1-*homoveratryl*-5 : 6-*dimethoxyindene* respectively:



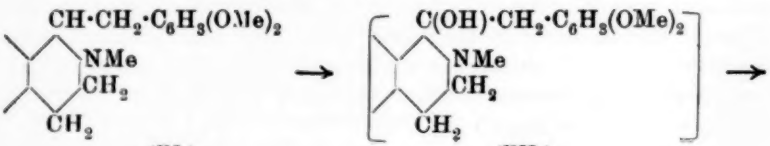
[R = OH, Cl or OMe].

The latter compound, $C_{21}H_{24}O_5$, yields on oxidation with potassium permanganate two neutral *compounds*, $C_{21}H_{24}O_7$ and $C_{21}H_{22}O_7$, a *monocarboxylic acid*, $C_{21}H_{24}O_8$, and a *dicarboxylic acid*, $C_{21}H_{24}O_9$. These substances have not been examined in detail, but probably represent stages in the oxidation of the unsaturated linking, as follows:

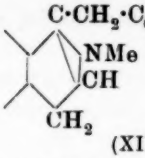




The view with regard to the constitution of pavine suggested above is thus shown to afford a satisfactory explanation of its behaviour on degradation. It is also capable of explaining the formations of pavine and its methyl derivative by the oxidation of tetrahydropapaverine and laudanosine respectively, and of throwing some light on the mechanism of the oxidation of 1-benzyl-2-alkyltetrahydro*iso*quinolines. The first stage in the oxidation of laudanosine (XI) would appear to be the introduction of an hydroxyl group in the 1-position of the *iso*quinoline nucleus, yielding the substance (XII). Some proportion of this then suffers internal condensation by the elimination of the elements of water between the 1-hydroxyl group and a hydrogen atom in the 3-position, yielding *N*-methylpavine (XIII):



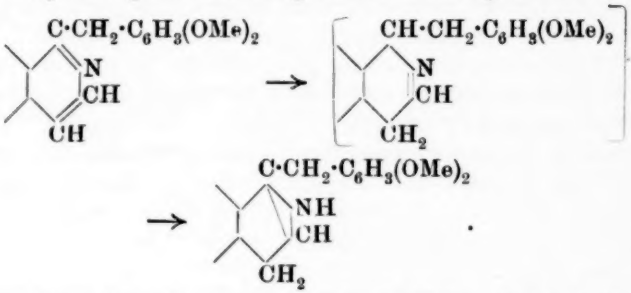
(XI.) (XII.)



(XIII.)

The major portion of (XII), however, suffers further oxidation, with formation of veratraldehyde and 6:7-dimethoxy-2-methyl-3:4-dihydro*iso*quinolinium hydroxide (Pyman, T., 1909, **95**, 1266).

The formation of pavine by the reduction of papaverine may conceivably take place according to the following scheme:



The author has pleasure in acknowledging the fact that the correct interpretation of these results was first suggested to him by Mr. M. Barrowcliff, to whom he desires to express his thanks.

Experimental.

N-*Methylpavinemethine*, $C_{22}H_{27}O_4N$.
(1-*Homoveratryl*-1-*dimethylamino*-5:6-*dimethoxyindene*).

Nineteen grams of *N*-methylpavine methiodide (containing $4H_2O$) (T., 1910, **97**, 1326) were dissolved in 150 c.c. of boiling water, and digested with the silver hydroxide, prepared from 6·0 grams of silver nitrate, until the liquor contained no iodide. The silver iodide was then removed by filtration, and the liquor boiled for three hours with 100 grams of 50 per cent. aqueous potassium hydroxide. The oil, which gradually separated, solidified to a varnish on cooling, and was removed by extraction with ether. The alkaline liquor was again boiled with another 100 grams of 50 per cent. aqueous potassium hydroxide, when a further small quantity of oil separated. This was again dissolved in ether, and the two ethereal extracts were then combined, dried with potassium carbonate, and distilled. The resulting oil was dissolved in absolute alcohol, and neutralised with concentrated hydrochloric acid (3·0 c.c.); after a short time colourless needles separated, and these were purified by recrystallisation from alcohol, giving

12·1 grams of the methine hydrochloride, melting at 205—206° (corr.).

This represents 83 per cent. of the theoretical. Better yields were obtained when working with large quantities; thus, 100 grams of *N*-methylpavine hydrochloride were converted into the methiodide, and the crude product was treated as described above, when 70 grams of the methine hydrochloride and 5 grams of *N*-methylpavine hydrochloride were recovered. This yield amounts to 90 per cent. of the theoretical. The separation of the methine hydrochloride and of *N*-methylpavine hydrochloride depends on the fact that the former crystallises from alcohol, but not from aqueous solutions, whilst the latter readily crystallises from water.

N-*Methylpavinemethine*.—On precipitating this base from a dilute solution of its hydrochloride with ammonia, it separates at first as an apparently amorphous powder. On keeping, however, this becomes distinctly crystalline, forming shimmering crystals, which, when collected and allowed to dry in the air, become a horny mass which has no definite melting point, gradually sintering together and becoming liquid at 50—95° (corr.). In this state it contains $2H_2O$.

Found, C = 65·2; H = 7·7.

$C_{22}H_{27}O_4N,2H_2O$ requires C = 65·1; H = 7·7 per cent.

On extracting the base from an aqueous suspension with chloroform, removing the greater part of the solvent by distillation, and the remainder by evaporation with alcohol, the base remains as a nearly colourless varnish. When this is dissolved in a little ether, and water is cautiously added, the hydrated base separates, on scratching, as a white, chalky solid, or in radial clusters of short, white needles. After thorough drying in the air it has the same melting point and composition as the precipitated base.

Found, C = 65·4; H = 7·8.

Found in base dried at 100°, C = 71·7; H = 7·4.

$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3 per cent.

This base is very sparingly soluble in water or light petroleum, sparingly so in ether, but readily so in the other usual organic solvents.

The *hydrochloride* crystallises from alcohol in glistening, prismatic needles, which contain $1\frac{1}{2}H_2O$, and, after drying at 100°, melts at 205—206° (corr.). It is readily soluble in cold water or hot alcohol.

Found, in air-dried salt, C = 61·5, 61·2; H = 7·5, 7·6; H_2O = 6·0.

$C_{22}H_{27}O_4N,HCl,1\frac{1}{2}H_2O$ requires C = 61·0; H = 7·2; H_2O = 6·2 per cent.

Found, in salt dried at 100°, C=64·9; H=7·2; Cl=8·6.

$C_{22}H_{27}O_4N,HCl$ requires C=65·1; H=7·0; Cl=8·7 per cent.

The *aurichloride* crystallises from a mixture of acetone and absolute alcohol in rust-brown fragments, which decompose at 156° (corr.). It is very sparingly soluble in water or alcohol, but fairly readily so in acetone. It is anhydrous.

Found, C=37·3; H=4·1; Au=27·8.

$C_{22}H_{27}O_4N,HAuCl_4$ requires C=37·2; H=4·0; Au=27·8 per cent.

The *picrate* crystallises from absolute alcohol in clear, yellow, prismatic needles, which melt at 195—196° (corr.).

Found, C=56·4; H=5·3.

$C_{22}H_{27}O_4N,C_6H_3O_7N_3$ requires C=56·2; H=5·1 per cent.

The *methiodide* separates in clusters of yellow plates when a methyl alcoholic solution of the anhydrous methine is mixed with a slight excess of methyl iodide and allowed to remain in the cold, the yield being more than 90 per cent. of the theoretical. This salt melts at 174—175° (corr.), and its melting point remains the same after quick crystallisation from methyl alcohol, although it then sinters a degree earlier.

This salt is sparingly soluble in water, methyl alcohol, or alcohol, somewhat sparingly so in acetone, but readily so in chloroform.

Found, loss at 100°=2·4.

$C_{22}H_{27}O_4N,CH_3I,\frac{1}{2}H_2O$ requires H_2O=1·7 per cent.

Found, in salt dried at 100°, C=53·6, 53·5; H=6·1, 6·0; I=25·0.

$C_{22}H_{27}O_4N,CH_3I$ requires C=54·0; H=5·9; I=24·8 per cent.

This salt has also been obtained in a hydrated form containing $2\frac{1}{2}H_2O$. (Found, H_2O=8·7. Calc., H_2O=8·1 per cent.) This form melts at 165—167° (corr.).

An aqueous solution of the methine methiodide gives no precipitate with aqueous sodium carbonate. The methine methiodide is easily decomposed by heating with water or methyl alcohol.

Oxidation of N-*Methylpavinemethine.*

Five grams of the hydrated methine hydrochloride were converted into the base, and this was dissolved in 250 c.c. of water and sufficient sulphuric acid. After adding 100 grams of ice, a solution of 5 grams of potassium permanganate in 250 c.c. of water, also cooled by the addition of 100 grams of ice, was run in, with thorough stirring. The temperature remained at 5° to 7°, and the permanganate was immediately decolorised. After keeping overnight, the liquor was filtered, and evaporated under diminished pressure to a volume of about 50 c.c., mixed with 20 c.c. of concentrated hydrochloric acid, and shaken with chloroform. After a

short time, the separation of a crystalline substance commenced, and this was eventually collected and washed with chloroform. The moist mass was dissolved in a little hot water, and kept in a vacuum desiccator over sulphuric acid, when 2·9 grams of the hydrochloride of $C_{22}H_{27}O_8N$ crystallised in large, prismatic needles. This yield is 51 per cent. of that theoretically possible.

The *dicarboxylic acid* was prepared by adding aqueous sodium carbonate to a concentrated aqueous solution of the hydrochloride until the liquor was no longer acid to methyl-orange, when the acid slowly crystallised on stirring. The crude product was purified by crystallisation from water, and formed colourless, prismatic needles containing $5H_2O$. The air-dried salt sintered at 80—100°, and melted with effervescence at 205—206° (corr.); after drying at 100°, however, it gradually melted in the neighbourhood of 150°.

Found, in air-dried salt, C = 51·3; H = 7·4; H_2O = 16·8.
$C_{22}H_{27}O_8N,5H_2O$ requires C = 50·5; H = 7·3; H_2O = 17·2 per cent.

Found, in salt dried at 100°, C = 60·9, 60·7; H = 6·4, 6·4.
$C_{22}H_{27}O_8N$ requires C = 60·9; H = 6·3 per cent.

On titration, 0·2602 of the air-dried substance required 5·0 c.c. of *N*/10-KOH, using phenolphthalein, whence the equivalent is 520. $C_{22}H_{27}O_8N,5H_2O$, functionating as a monobasic acid, requires equivalent = 523. The acid is readily soluble in hot water, but sparingly so in cold water or alcohol.

The *hydrochloride* crystallises from a concentrated aqueous solution in prismatic needles, which, after drying, effervesce first at 178° and then at 212° (corr.). It is very readily soluble in water or alcohol, giving a strongly acid solution, but sparingly so in cold acetone. The air-dried salt contains $1H_2O$, which is not lost at 100°.

Found, in salt dried at 100°, C = 54·0, 54·1; H = 6·2, 6·3; Cl = 7·4.
$C_{22}H_{27}O_8N,HCl,H_2O$ requires C = 54·1; H = 6·2; Cl = 7·3 per cent.

The *aurichloride* crystallises from a mixture of acetone and alcohol in clusters of hard, yellow prisms, which decompose at 240° (corr.). It is anhydrous, and is very sparingly soluble in water or alcohol, but readily so in acetone.

Found, C = 34·4, 34·4; H = 3·7, 3·8; Au = 25·6.
$C_{22}H_{27}O_8N,HAuCl_4$ requires C = 34·1; H = 3·7; Au = 25·5 per cent.

The *picrate* crystallises from absolute alcohol in beautiful yellow plates, which melt and effervesce at 137° (corr.) when freshly prepared, or after drying at a temperature of 100°; on exposure to the air it absorbs moisture, and melts at a temperature a few degrees lower. It is very sparingly soluble in water, and sparingly so in alcohol.

Found, in salt dried at 100°, C=50·9, 50·6; H=5·0, 5·0.
$C_{22}H_{27}O_8N,C_6H_3O_7N_3$ requires C=50·7; H=4·6 per cent.

Action of Boiling Methyl Alcohol on N-*Methylpavinemethine Methiodide.*

Thirty grams of the methine methiodide (containing 8·7 per cent. H_2O) and 60 c.c. of methyl alcohol were boiled for one hour under a reflux condenser. The methiodide dissolved completely in the alcohol in the course of about ten minutes. On cooling, a quantity of white crystals separated, and, after removing these, the mother liquor gave on evaporation a partly crystalline residue. The crystals and residue were combined, and extracted with warm water until the extracts no longer contained iodide. The colourless, insoluble, crystalline powder was crystallised from methyl alcohol, and gave 12·1 grams of prismatic needles (m. p. 130—131°), 5·4 grams of prismatic needles (m. p. 124—130°), and 1·4 grams of indefinite crystals (m. p. 120—130°). The total yield, 18·9, closely approaches the calculated quantity (19·2 grams) of the substance, $C_{21}H_{24}O_5$, obtainable.

The aqueous mother liquor was evaporated to dryness, and gave 9·7 grams of trimethylamine hydriodide, instead of 10·1 grams theoretically possible.

The identity of this salt was established by its melting point, 265° (corr.), with decomposition, and analysis (Found, C=19·9; H=5·6. Calc., C=19·3; H=5·3 per cent.), and by the melting point, 250° (corr.), and analysis of the aurichloride prepared from it. (Found, C=9·4; H=2·8; Au=49·4. Calc., C=9·0; H=2·5; Au=49·4 per cent.)

1-*Homoveratryl*-1 : 5 : 6-*trimethoxyindene*, $C_{21}H_{24}O_5$.

This substance crystallises from methyl alcohol in clusters of prismatic needles, which melt at 130—131° (corr.), after softening earlier. It suffers no loss at 100°.

Found, C=70·3, 70·6, 70·9, 70·6; H=6·9, 6·9, 6·8, 6·9; OMe=43·4, 43·9.
$C_{21}H_{24}O_5$ requires C=70·8; H=6·8; 5OMe=43·6 per cent.

The molecular weight was determined by the cryoscopic method in benzene:

0·1808	in 16·25	benzene gave	Δ −0·165°.	M.W.=330.
0·4003	„ 16·25	„ „	Δ −0·365°.	M.W.=331.
0·2314	„ 19·50	„ „	Δ −0·180°.	M.W.=323.
0·3377	„ 19·50	„ „	Δ −0·260°.	M.W.=326.

$C_{21}H_{24}O_5$ requires M.W.=356.

This substance is insoluble in water, very sparingly so in ether or light petroleum, but readily so in the other usual organic solvents on warming. It readily decolorises bromine or potassium permanganate.

On oxidation of a solution of 1 gram in 100 c.c. of acetone with 2 grams of potassium permanganate in 200 c.c. of water at about 10°, a variety of products have been obtained, the results being somewhat capricious; on some occasions a neutral substance, $C_{21}H_{22}O_7$, melting at 170—172° (corr.), and a mixture of acids consisting chiefly of a dicarboxylic acid, $C_{21}H_{24}O_9$, melting at 206—207° (corr.), have been isolated; on others, a neutral substance, $C_{21}H_{24}O_7$, melting at 141—142° (corr.), and a monocarboxylic acid, $C_{21}H_{24}O_8$, melting at 220—222° (corr.), have been isolated. When a larger excess (4 parts) of potassium permanganate is employed, the product consists mainly of the dicarboxylic acid, $C_{21}H_{24}O_9$.

The properties of the oxidation products are as follows:

Neutral substance, $C_{21}H_{24}O_7$, crystallises from methyl alcohol in very pale yellow, prismatic needles, melting at 141—142° (corr.).

Found, C = 64·6, 64·8, 64·8; H = 6·3, 6·6, 6·2.

$C_{21}H_{24}O_7$ requires C = 64·9; H = 6·2 per cent.

Neutral substance, $C_{21}H_{22}O_7$, crystallises from alcohol in pale yellow clusters of prismatic rods, which melt to a yellow liquid at 170—172° (corr.).

Found, C = 65·4, 65·0, 65·1; H = 5·8, 5·9, 6·0.

$C_{21}H_{22}O_7$ requires C = 65·3; H = 5·8 per cent.

Monocarboxylic acid, $C_{21}H_{24}O_8$, crystallises from glacial acetic acid in colourless clusters of glistening prisms, which soften at 210° and melt at 220—222° (corr.).

Found, C = 62·2, 61·9; H = 6·2, 6·0; equivalent = 394.

$C_{21}H_{24}O_8$ requires C = 62·3; H = 6·0 per cent. M.W. = 404.

Dicarboxylic acid, $C_{21}H_{24}O_9$, crystallises from glacial acetic acid or benzene in needles, and from methyl alcohol in clusters of colourless plates, which melt at 206—207° (corr.), then lose gas, resolidify, and melt again at about 270°.

Found, C = 59·5, 60·1, 59·5; H = 5·7, 5·9, 5·7; OMe = 35·5, 35·5; equivalent = 215, 214.

$C_{21}H_{24}O_9$ requires C = 60·0; H = 5·8; 5OMe = 36·9 per cent. M.W. = 420.

It is insoluble in water or dilute acids, but readily soluble in sodium carbonate. It is sparingly soluble in cold alcohol or acetic acid or hot benzene, but fairly readily so in [illegible] alcohol or acetic acid.

Action of Boiling Water on N-*Methylpavinemethine Methiodide. Formation of* 1-*Hydroxy*-1-*homoveratryl*-5 : 6-*dimethoxyindene.*

Twenty grams of the methine methiodide were added to 200 c.c. of boiling water. The solution was at first almost clear, but rapidly became turbid, owing to the deposition of an oil. After seeding, and keeping in the water-bath for two hours, the separated matter, which had become crystalline, was collected, and the aqueous liquor evaporated to dryness, giving 5·8 grams of trimethylamine hydriodide, decomposing at 265°. The insoluble matter was dried in the air, and crystallised first from benzene, when 8·0 grams, melting at 143°, were obtained. After subsequent crystallisations from ethyl acetate and alcohol, it was obtained in clusters of colourless needles, which melted at 147—148° (corr.).

Found, C = 69·9, 70·1; H = 6·6, 6·5; OMe = 36·9; 35·5.

$C_{20}H_{22}O_5$ requires C = 70·1; H = 6·5; 4OMe = 36·3 per cent.

This substance is insoluble in water, sparingly soluble in hot or cold ether, and in cold alcohol, ethyl acetate, or benzene. On distillation of its solutions in organic solvents, it frequently remains in an amorphous state as a gum.

1-*Chloro*-1-*homoveratryl*-5 : 6-*dimethoxyindene*, $C_{20}H_{21}O_4Cl$.—When either pure, crystalline 1-hydroxy-1-homoveratryl-5 : 6-dimethoxyindene or its amorphous form, to which reference has been made above, is mixed with 3 parts of acetyl chloride, boiled for a few minutes under a reflux condenser, and evaporated to dryness, a crystalline residue remains, which, after stirring with acetone, melts at 218—220° (corr.). It crystallises from glacial acetic acid in prismatic needles, having the same melting point. It is insoluble in water, very sparingly soluble in hot ether, alcohol or ethyl acetate, or in cold glacial acetic acid, but soluble to the extent of about 4 per cent. in boiling glacial acetic acid.

Found, C = 66·4, 66·3; H = 6·1, 6·0; Cl = 9·9; OMe = 33·0, 33·6.

$C_{20}H_{21}O_4Cl$ requires C = 66·6; H = 5·9; Cl = 9·8.

4OMe = 34·3 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

[*Received, Jan. 21st*, 1915.]

XX.—*Osmotic Pressure of Alcoholic Solutions. Part I. Vapour Pressures and Densities.*

By Tudor Williams Price.

Measurements of osmotic pressure in aqueous solutions over a considerable range of concentration and temperature have been carried out by several investigators, notably Pfeffer, Morse and his co-workers, and Lord Berkeley and Hartley, but very few determinations have been made for non-aqueous solutions. Kahlenberg (*J. Physical Chem.*, 1906, **10**, 141; 1909, **13**, 93), Cohen and Commelin (*Zeitsch. physikal. Chem.*, 1908, **64**, 1), and Wilcox (*J. Physical Chem.*, 1910, **14**, 576) measured the osmotic pressure of pyridine solutions, using membranes of rubber. The results, however, were conflicting.

It was considered advisable to carry out a systematic investigation of the osmotic pressure of alcoholic solutions over a large range of concentration at various temperatures. In view of the manipulative difficulties and the difficulty of obtaining a truly semipermeable membrane, the indirect method was employed. The validity of this method depends on the fact that the osmotic pressure of a solution is a measure of the diminution of the free energy of a solvent by the addition of a solute, or a measure of the work done in separating the solvent from the solution. These can be determined experimentally by methods which do not involve ordinary membranes. One of the most important indirect methods is the determination of the vapour pressure of the solvent and solution. This indirect determination of osmotic pressure is analogous to that carried out directly with precipitation membranes, because the surface layer of the solution in contact either with the vapour or with the solvent acts as a semipermeable membrane, since it allows the passage of the solvent, but not of the solute, molecules.

The relation between the osmotic pressure and vapour pressure of a solution for liquids of any degree of compressibility has been worked out by Porter (*Proc. Roy. Soc.*, 1907, [*A*], **79**, 519; 1908, [*A*], **80**, 457). Berkeley, Hartley and Burton (*Phil. Trans.*, 1908, [*A*], **209**, 177) modified the equation so that it could be made applicable to measurements carried out in air, and they deduce a formula by which the osmotic pressure of a solution can be calculated from the vapour pressure, the density, and the compressibility of the solution. The values obtained by Berkeley and his co-workers by this indirect method are in excellent agreement with

those obtained directly by them, thus showing that their formula is capable of giving accurate results.

In the present paper an account is given of the determination of the vapour pressure and density of alcoholic solution of carbamide and nitrobenzene. The latter substance was chosen, in spite of its slight volatility at the temperatures used, because very concentrated solutions were desired. Measurements were made with carbamide solutions at 40°, 50°, 60°, and 70°, and with nitrobenzene solutions at 20°, 30°, 40°, 50°, and 60°.

The range of concentration was from 15 to 60 grams of solute per litre of solvent for carbamide, and from 60 to 3000 grams of solute per litre of solvent for nitrobenzene.

Work is now in progress on the compressibilities of the solutions.

Experimental.

Purification of Materials.—Absolute alcohol was obtained by boiling rectified spirit over lime under a reflux condenser until all the lime was broken up, and subsequent distillation. This was repeated, and the alcohol then treated twice in a similar manner with 1 per cent. of its weight of freshly-turned calcium.

The carbamide was recrystallised from distilled water and carefully dried.

The nitrobenzene was purified by repeated fractional distillation.

Method of Work.

(*a*) *Vapour Pressures.*—The determinations of vapour pressure were made by the air-current method. The apparatus used, and the method of procedure, were the same as those described by Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, 68).

A known volume of dry air was bubbled through a series of three bulbs, containing alcohol or solution, placed in a thermostat. The alcohol vapour taken up by the air was absorbed by being passed through concentrated sulphuric acid, and weighed.

Then, if w = weight of alcohol vapour withdrawn,
P = pressure in last bulb,
p = pressure in aspirator,
T = temperature of water in aspirator (°A),
V = volume in litres of air aspirated,
v_a = specific volume of alcohol vapour $= \frac{22{\cdot}41}{M}$,
M = molecular weight of alcohol,

assuming that Dalton's law of partial pressures is true and that

the density of alcohol vapour is normal, the following relationship holds good:

$$\frac{\text{Pressure of alcohol vapour}}{\text{Total pressure}} = \frac{\text{Volume of alcohol vapour}}{\text{Total volume}}.$$

or

$$\frac{p_a}{P} = \frac{w \,.\, v_a}{V + w \,.\, v_a}.$$

Correcting V for temperature and pressure, we obtain

$$p_a = \frac{w \,.\, v_a \; T.P. \; 760}{273 \, p \,.\, V + 760. \;\; w \,.\, v_a \,.\, T},$$

that is, vapour pressure=

$$\frac{w \times 0{\cdot}4872 \times 760 \times T \times P}{273 \times p \times V + w \times 0{\cdot}4872 \times 760 \times T}.$$

The rate of aspiration was varied largely, but without appreciable difference in the results. The one eventually adopted was about 1 litre in half an hour.

The thermostat was heated electrically, and the temperature kept constant by means of an electric regulator. The temperature did not vary more than one-fiftieth of a degree during an experiment.

The complete absorption of the alcohol vapour by the sulphuric acid was proved as follows. After passing through the sulphuric acid, the air was passed through a bulb containing an aqueous solution of iodine and potassium hydroxide. No trace of iodoform was found at the end of the experiment.

An experiment was also performed to determine the volatility of nitrobenzene at the higher temperatures. The bulbs were filled with pure nitrobenzene at 60°, and 4 litres of air passed through. It was found that the increase in weight of the sulphuric-acid bulb was equivalent to a vapour pressure of 1·1 mm., equal to about 0·3 per cent., so that the error introduced by this did not amount to more than 0·2 per cent. even for the most concentrated solution of nitrobenzene at the highest temperature.

(*b*) *Densities.*—The densities were determined by means of a 50 c.c. density bottle suspended in the thermostat. The latter had one glass side, so that by placing an electric lamp behind the bottle, the level of the liquid in the bottle could easily be seen through a cathetometer. The capacity of the bottle at each temperature was determined by means of distilled water, which had previously been boiled to remove dissolved air.

The vapour pressure and density were determined simultaneously for each solution.

The experimental data for alcohol at 20°, 30°, 40°, 50°, 60°, and 70°, and for carbamide solutions at 40°, are as follows: W represents the weight of alcohol absorbed, P the pressure in

the last bulb, p the pressure in the aspirator, T the temperature of the aspirator, and V the volume of air drawn through. D is the density of the solution. The concentration is denoted by $\frac{n}{N}$, the ratio of the molecules of solute and solvent.

Vapour Pressure and Density of Alcohol.

20°. $V = 4{\cdot}0$ litres.

P. mm.	W. gram.	T. (°A).	p. mm.	Vapour pressure, mm.	D.
763·7	0·4755	283·2	750·9	43·80	0·79085
762·0	0·4775	283·75	748·9	44·00	0·79086

30°. $V = 2{\cdot}0$ litres.

757·2	0·4467	285·35	743·0	78·89	0·78034
754·9	0·4457	285·9	740·3	78·90	0·78039

40°. $V = 1{\cdot}0$ litre.

760·4	0·4003	293·55	738·3	135·0	0·77303
760·0	0·3995	293·8	737·8	134·9	0·77299

50°. $V = 1{\cdot}0$ litre.

760·0	0·7975	287·8	741·0	224·8	0·76309
759·7	0·7957	288·0	739·6	224·8	0·76291

60°. $V = 0{\cdot}5$ litre.

743·55	0·8314	289·5	723·5	352·7	0·75408
748·6	0·8292	289·0	729·0	352·8	0·75405

70°. $V = 0{\cdot}5$ litre.

751·4	2·4340	288·9	734·0	542·6	0·74620
751·9	2·4291	289·05	734·4	542·6	0·74620

Carbamide at 40°. $V = 1{\cdot}0$ litre.

P. mm.	W. gram.	T. (°A).	p. mm.	Vapour pressure, mm.	D.	n/N.
756·1	0·4055	287·1	740·1	133·0	0·77839	0·01168
755·8	0·4050	287·4	739·6	133·0	0·77846	
756·6	0·3856	294·1	734·1	131·1	0·78525	0·02367
756·2	0·3853	294·25	733·4	131·1	0·78528	
757·8	0·3810	293·0	737·0	129·1	0·79150	0·03552
757·3	0·3829	293·2	736·3	129·5	0·79152	
755·7	0·3739	293·75	734·0	127·5	0·79722	0·04771
755·7	0·3718	293·8	734·0	126·9	0·79723	

Results.—The following results have been obtained for alcohol at the temperature stated. The results for the vapour pressure of other workers are given for the sake of comparison:

		Vapour Pressure in mm.				
Temperature.	Density.	Price.	Merriman.*	Ramsay and Young.†	Regnault.†	Schmidt.†
20°	0·79085	43·9	43·8	44·00	44·46	43·7
30	0·78037	78·9	78·6	78·06	78·52	78·0
40	0·77301	134·95	134·9	133·42	133·69	133·8
50	0·76300	224·8	222·2	219·82	219·90	220·9
60	0·75405	352·8	352·7	350·2	350·21	352·1
70	0·74620	542·6	542·5	540·9	541·15	543·0

* T., 1913, **103**, 628. † From Landolt and Börnstein's "Tabellen."

The results for carbamide and nitrobenzene solutions are given in the following tables. The concentration of the solutions is expressed as $\frac{n}{N}$, the ratio of the molecules of solute and solvent respectively. *V.P.* is the vapour pressure of the solutions, and $p-p'$ is the depression of vapour pressure, using the author's results for the vapour pressure of absolute alcohol.

The results given are the mean of two determinations for each solution at each temperature.

M is the molecular weight calculated from the formula

$$M = \frac{p'}{p-p'} \cdot \frac{46\,w}{W},$$

where w is weight of solute, W the weight of solvent, 46 the molecular weight of the solvent (alcohol), p the vapour pressure of the solvent, and p' that of the solution.

The osmotic pressures are calculated from the formula

$$P - \tfrac{1}{2}\beta P^2 = \frac{RT}{V_0} \cdot \log_e \frac{p}{p'},$$

where P is the osmotic pressure, β the coefficient of compressibility of the solvent, and V_0 the molecular volume of the solvent. p and p' have the same meaning as in the preceding paragraph.

The values of β used are those given by Tyrer (T., 1913, **103**, 1686).

Carbamide at 40°.

n/N.	*V.P.*	$p-p'$.	Density.	*M*.	Osmotic pressure.
0·01167	133·0 mm.	1·95 mm.	0·77843	47·4	6·28 atmos.
0·02367	131·1 ,,	3·85 ,,	0·78526	48·4	12·83 ,,
0·03552	129·3 ,,	5·65 ,,	0·79151	48·8	18·46 ,,
0·04771	127·2 ,,	7·75 ,,	0·79722	47·0	25·54 ,,

Carbamide at 50°.

n/N.	$V.P.$	$p-p'$..	Density.	M.	Osmotic pressure.
0·01171	221·55 mm.	3·25 mm.	0·77115	47·9	6·40 atmos
0·02355	218·3 „	6·5 „	0·77696	47·5	12·90 „
0·03587	214·9 „	9·9 „	0·78278	46·7	19·80 „
0·04781	211·5 „	13·3 „	0·78820	45·6	26·83 „

Carbamide at 60°.

0·01154	347·7 mm.	5·1 mm.	0·76232	49·7	6·51 atmos.
0·02340	342·7 „	10·1 „	0·76813	47·6	13·01 „
0·03565	337·5 „	15·3 „	0·77389	47·1	19·86 „
0·04773	332·1 „	20·7 „	0·77895	45·9	27·10 „

Carbamide at 70°.

0·01175	534·9 mm.	7·7 mm.	0·75190	48·9	6·56 atmos.
0·02355	527·2 „	15·4 „	0·75751	46·2	13·14 „
0·03582	519·1 „	23·5 „	0·76331	47·5	20·22 „
0·04792	510·95 „	31·65 „	0·76850	46·4	27·46 „

Nitrobenzene at 20°.

0·02339	43·03 mm.	0·87 mm.	0·80832	107·7	8·27 atmos.
0·05118	42·14 „	1·76 „	0·82727	150·7	16·91 „
0·08576	41·37 „	2·53 „	0·84860	172·5	24·54 „
0·12518	40·57 „	3·33 „	0·86971	187·6	32·62 „
0·16905	39·97 „	3·93 „	0·89039	211·5	38·80 „
0·21908	39·49 „	4·41 „	0·91086	241·3	43·82 „
0·29860	39·00 „	4·90 „	0·93817	292·3	49·00 „
0·42056	38·36 „	5·54 „	0·97140	350·0	55·87 „
0·62683	37·72 „	6·18 „	1·01193	470·6	62·85 „
1·0756	36·84 „	7·06 „	1·06458	690·4	72·68 „

Nitrobenzene at 30°.

0·02425	77·12 mm.	1·78 mm.	0·79824	129·2	9·61 atmos.
0·05134	75·78 „	3·12 „	0·81666	153·4	17·01 „
0·08655	74·27 „	4·63 „	0·83789	170·8	25·51 „
0·12668	72·90 „	6·00 „	0·85943	189·3	33·39 „
0·17050	71·68 „	7·22 „	0·88045	208·2	40·72 „
0·21983	70·67 „	8·23 „	0·90078	232·2	46·55 „
0·29694	69·36 „	9·54 „	0·92767	265·5	54·47 „
0·42224	68·16 „	10·74 „	0·96177	329·6	61·87 „
0·62575	66·68 „	12·22 „	1·00178	420·0	71·20 „
1·0885	64·60 „	14·29 „	1·05556	605·4	84·61 „

Nitrobenzene at 40°.

0·02451	131·4 mm.	3·55 mm.	0·79104	111·6	11·50 atmos
0·05142	129·25 „	5·70 „	0·80892	142·1	18·63 „
0·08636	126·9 „	8·05 „	0·82985	165·3	26·56 „
0·12539	124·45 „	10·50 „	0·85081	182·8	34·22 „
0·16818	122·85 „	12·10 „	0·87059	210·0	40·60 „
0·22138	121·0 „	13·95 „	0·89250	236·2	47·14 „
0·29855	118·7 „	16·25 „	0·91890	268·2	55·51 „
0·41925	116·5 „	18·45 „	0·95185	325·6	63·63 „
0·61284	114·0 „	20·95 „	0·99071	410·2	73·06 „
1·1057	109·5 „	25·45 „	1·04756	585·1	90·61 „

Nitrobenzene at 50°.

n/N.	*V.P.*	$p-p'$.	Density.	*M*.	Osmotic pressure.
0·02484	219·1 mm.	5·7 mm.	0·78089	117·4	12·06 atmos.
0·05331	215·4 „	9·4 „	0·79928	146·5	18·76 „
0·08562	211·5 „	13·3 „	0·81898	167·5	26·81 „
0·12439	207·9 „	16·9 „	0·83969	188·2	34·40 „
0·17078	204·5 „	20·3 „	0·86096	221·3	41·68 „
0·21829	201·55 „	23·25 „	0·88104	232·8	48·10 „
0·29642	197·9 „	26·9 „	0·90811	268·5	56·30 „
0·40206	194·5 „	30·3 „	0·93795	316·7	63·85 „
0·61379	188·5 „	36·3 „	0·98101	392·0	77·73 „
1·0888	178·6 „	46·2 „	1·03624	517·8	101·70 „

Nitrobenzene at 60°.

0·02363	344·0 mm.	8·8 mm.	0·77182	113·6	11·31 atmos.
0·05187	338·3 „	14·5 „	0·79097	148·9	18·80 „
0·08588	332·3 „	20·5 „	0·81087	172·0	26·84 „
0·12479	326·6 „	26·2 „	0·83148	191·3	34·61 „
0·16704	321·5 „	31·3 „	0·85217	210·0	41·69 „
0·21311	316·8 „	36·0 „	0·87163	231·2	48·33 „
0·29409	311·15 „	41·65 „	0·89948	262·7	56·44 „
0·41626	302·8 „	50·0 „	0·93280	310·1	68·72 „
0·62371	294·8 „	58·0 „	0·97342	389·9	80·83 „
1·11528	278·1 „	74·7 „	1·02453	487·7	107·24 „

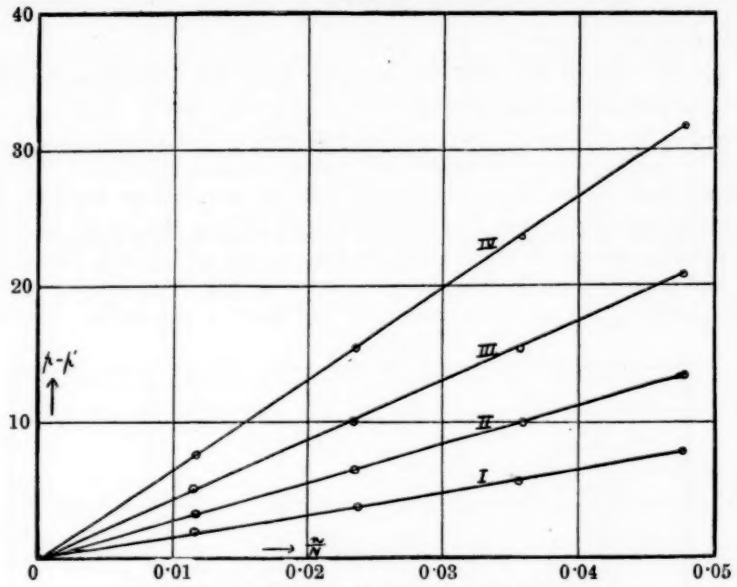
Discussion of Results.

Accurate determination of the vapour pressure of water and aqueous solutions can be made by the dynamical or air-bubbling method, as shown by the work of Walker, Regnault, Lord Berkeley, Perman and others. A comparison of the results obtained in this paper with those obtained by Regnault, Ramsay and Young, Schmidt, and Merriman (see above) affords evidence of the trustworthiness of this method for the determination of the vapour pressure of alcohol and of alcoholic solutions. The author's results are in good agreement with those quoted, notably with those of Merriman. Thus the assumptions made in developing the equation for calculating the vapour pressures, namely, that Dalton's law of partial pressures is true, and that the vapour density of alcohol vapour is normal, seem to be justified.

The lowering of vapour pressure, and the density, have been plotted against the corresponding concentrations, and are shown in the accompanying diagrams.

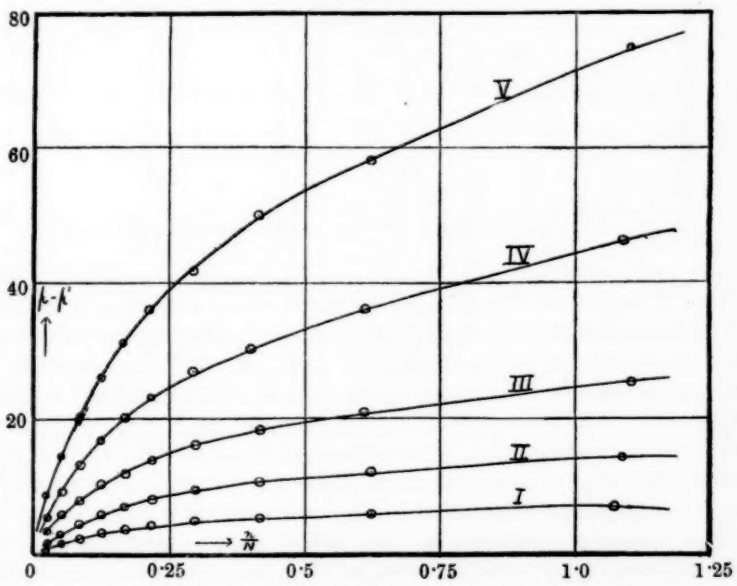
Owing to the great difference in the range of concentration ($\frac{n}{N}$=0·011 to 0·048 for carbamide solutions and 0·0234 to 1·115 for nitrobenzene solutions), it has not been found possible to include the curves for the two substances on the same diagram.

FIG. 1.



Curve I *is at* 40°, II *at* 50°, III *at* 60°, *and* IV *at* 70°.

FIG. 2.



Curve I *is at* 20°, II *at* 30°, III at 40°,-IV *at* 50°, *and* V *at* 60°.

Fig. 1 shows the relation between $\frac{n}{N}$ and $p—p'$ for carbamide solutions.

All the curves are straight, showing that the depression is proportional to the concentration.

Fig. 2 shows the relation between $\frac{n}{N}$ and $p—p'$ for nitrobenzene solutions.

Here also the curves are fairly straight within the limits of concentration shown on the carbamide curves, but afterwards the slope of the curves becomes less steep.

FIG. 3.

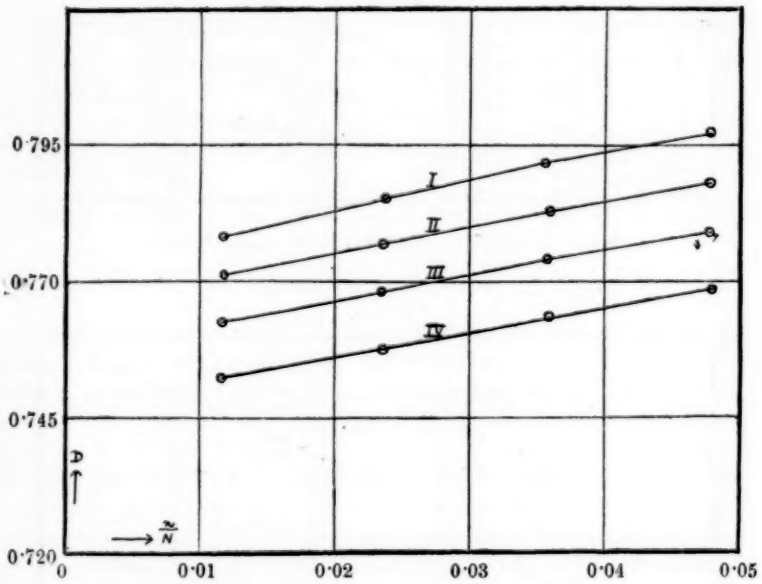


Fig. 3 represents the relation between concentration and density for carbamide solutions, and Fig. 4 for nitrobenzene solutions. The numbering is in each case the same as in the corresponding vapour-pressure curves. The curves are nearly straight for small differences in concentration, and are regular and parallel to each other for each substance. The difference in density for each degree centigrade is the same for carbamide and nitrobenzene solutions over a large range of concentration, and is about 0·00095.

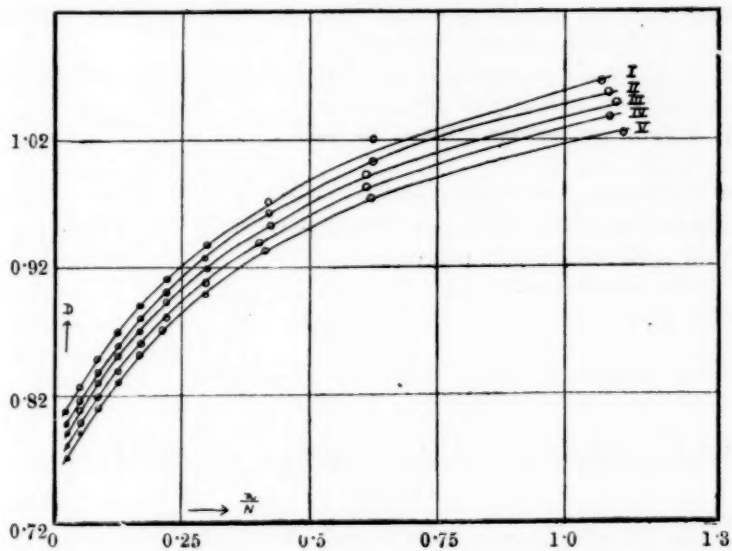
The osmotic pressure, as calculated above, increases as the temperature of the solution is raised, but is not proportional to the absolute temperature. At higher temperatures it is less than that

calculated from lower temperatures according to direct proportionality.

Babo's law, according to which $\frac{p-p'}{p}$ is independent of temperature, has been tested by means of the figures obtained in this work. A certain concentration was taken, and the depression of vapour pressure read from the curves at the different temperatures. This was repeated at different parts of the curves. It will be seen from the following figures that $\frac{p-p'}{p}$ is fairly constant for carbamide and nitrobenzene solutions.

For a carbamide solution of 0·01 concentration, the values of

FIG. 4.



$\frac{p-p'}{p}$ are 0·0118, 0·0119, 0·0122, and 0·0121 at 40°, 50°, 60°, 70° respectively, whilst the corresponding values for a solution of 0·04 concentration are 0·0482, 0·0494, 0·0490, and 0·0485.

For a nitrobenzene solution of 0·05 concentration, the values of $\frac{p-p'}{p}$ are 0·0410, 0·0406, 0·0408, 0·0414, and 0·0403 at 20°, 30°, 40°, 50°, 60° respectively, whilst the corresponding values for a solution of 0·25 concentration are 0·1048, 0·1103, 0·1089, 0·1108, and 0·1111.

In all cases the molecular weights, calculated from the diminution of vapour pressure, vary greatly from the theoretical. Carb-

amide solutions give an approximately constant molecular weight of about 47. In the case of nitrobenzene it increases gradually from 107 to 690. Thence it appears that the formula for calculating molecular weights by means of the depression of vapour pressure is not applicable to concentrated solutions.

Summary.

(1) Measurements have been made of the vapour pressures and densities of alcohol, and alcoholic solutions of carbamide and nitrobenzene at different temperatures.

(2) The agreement between the results of the vapour pressures of alcohol made by this method (air-bubbling) with those of other workers by other methods seems to justify the assumption that Dalton's law of partial pressures is true, and that the vapour density of alcohol vapour is normal.

(3) The osmotic pressures of the solutions have been calculated, using the compressibility of the solvent.

(4) Babo's law has been found to hold.

In conclusion, the author desires to thank Prof. W. J. Pope, F.R.S., for his kind advice and encouragement in the work.

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XXI.—*Addition of Auxochromes in the Flavone Group.*

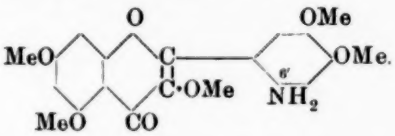
By ARTHUR GEORGE PERKIN and EDWIN ROY WATSON.

IN a former communication (Watson, T., 1914, **105**, 338), experiments were described which had as their object the introduction of an additional hydroxyl group into the quercetin molecule. By the methods employed, however, this could not be effected, because it was found impossible to convert aminoquercetin pentamethyl ether, by means of the diazo-compound, into the corresponding hydroxy-derivative. On the other hand, aminoquercetin was successfully prepared, and it was shown that the amino-group exerted but little effect on the tinctorial property of the dye.

With the same objects in view, namely, to deepen the colour of the dye and to prepare new polyhydroxyflavones which might prove of future service in the study of the natural members of this group,

identical methods have been applied to both luteolin and morin. Here, however, additional difficulties arise, for although quercetin can be obtained in quantity with comparative facility, the colouring matters in question, especially the former, are far from easy to isolate in quantity and in a pure condition. The work has consequently been hampered by a paucity of raw material.

Luteolin.—It was considered possible that the difficulty experienced in converting the aminoquercetin derivative into the corresponding hydroxy-compound was owing to the hydroxy-group already present in the pyrone ring:



Such an assumption would involve, in the case of aminoquercetin pentamethyl ether, a demethylation of the pyrone methoxy-group, and the formation of a diazo-oxide linking between this and the diazonium hydroxide, during the attempted decomposition of the latter. With morin, for instance, which contains the pyrone hydroxyl group and a hydroxyl group in the same position (6′) as this amino-group, an anhydro-sulphate (T., 1896, **59**, 1442) is readily produced, and this formation of an anhydro-compound apparently arises only when two hydroxyl groups are present in these positions.

In luteolin, the pyrone hydroxyl group is absent, and it is interesting to observe, whatever explanation of the anomaly may be forthcoming in the future, that there is no difficulty in preparing hydroxytetraethyl-luteolin from the corresponding diazo-derivative.

For the purpose of this investigation, the luteolin available was converted into the tetraethyl compound, because this is more economically prepared than the tetramethyl ether, and no material difference in the behaviour of these compounds was anticipated. Most probably this has been a mistake, because, although quercetin and morin pentamethyl ethers both readily yield a mononitro-compound, with luteolin tetraethyl ether under the most varied conditions of nitration a tetranitro-derivative could only be obtained. When opportunity occurs, the behaviour of luteolin tetramethyl ether under the same conditions will be studied.

The introduction of one nitro-group into luteolin tetraethyl ether was subsequently effected by means of the monobromo-derivative. With bromine in acetic acid solution, *bromoluteolin tetraethyl ether perbromide*, $C_{23}H_{25}O_6Br,HBr_3$, is produced, and this, on boil-

ing with water, yields a mixture of *bromoluteolin tetraethyl ether* and *tetrabromoluteolin tetraethyl ether*. When, however, one molecule of halogen is used, *bromoluteolin tetraethyl ether hydrobromide*, $C_{23}H_{25}O_6Br,HBr$, separates, which, on treatment with water, gives pure monobromoluteolin tetraethyl ether. From this, by nitration, *bromo-6′-nitroluteolin tetraethyl ether* could be prepared, which, on reduction, was converted into the corresponding *amino*-derivative. By diazotising, and subsequently boiling with water, *bromo-6′-hydroxyluteolin tetraethyl ether* was readily obtained.

The conversion of the latter compound into hydroxyluteolin would, it was anticipated, be a simple operation; but this, unfortunately, did not prove to be the case, and this compound has not been prepared in a pure condition. Thus, by the action of boiling hydriodic acid (D 1·7) for one hour only, two ethyl groups were apparently eliminated, and a compound, probably *bromo-6′-hydroxyluteolin diethyl ether*, was obtained. As incomplete deethylation had apparently been caused by the insolubility of the substance in hydriodic acid, a mixture of hydriodic acid and acetic anhydride was now employed, and there was thus produced a small amount of a substance, which was either an impure *6′-hydroxyluteolin* or 6′-hydroxyluteolin monoethyl ether. Although the analytical figures are somewhat too high, it is probable that the first supposition is correct, but, owing to the meagre amount available, no elaborate process of purification was possible. The matter is, however, reserved for further study, when it seems likely that, by the employment in the first place of luteolin tetramethyl ether, this desired compound will be more readily obtained.

The compound forms yellow needles, closely resembling luteolin itself, soluble in alkalis with a yellow colour, and no deepening of shade had occurred as the result of the introduction of the new hydroxyl group. When bromonitroluteolin tetraethyl ether is oxidised with permanganate, a *nitro*-3:4-*diethoxybenzoic acid* is produced, from which it is evident that the nitro-group is present in the catechol nucleus. Such an acid has not been previously prepared, but little doubt can exist that the nitro-group in bromonitroluteolin diethyl ether occurs in the 6′-position.

The course of bromination studied in the case of luteolin tetraethyl ether makes it probable from analogy that the compound previously described (*loc. cit.*) as dibromoquercetin pentamethyl ether hydrobromide is, in reality, *bromoquercetin pentamethyl ether perbromide*.

In certain cases, the colour of the compounds here described is interesting, being in marked contrast to the very similar deriv-

atives of quercetin. Thus, bromo-6′-nitro- and tetranitro-luteolin tetraethyl ethers are practically colourless, whereas 6′-nitro-quercetin pentamethyl ether is bright yellow. Again, bromo-6′-aminoluteolin tetraethyl ether and its hydrochloride are bright yellow, the latter becoming scarlet in a vacuum, whereas the stannichloride, $(C_{23}H_{26}O_6NBr)_4,H_4SnCl_6$, is deep crimson. On the other hand, 6′-aminoquercetin pentamethyl ether and its hydrochloride are almost white. There is possibly some similarity between the scarlet and crimson derivatives of fully ethylated flavones (see also Watson, *loc. cit.*, pp. 339, 346, 347) and the coloured hydrochlorides of styryl methyl ketone and other unsaturated aromatic ketones described by Francesconi and Cusmano (*Gazzetta*, 1908, **38**, ii, 70). In this connexion, attention may also be drawn to the deep red phenyl piperidylstyryl ketone previously described (T., 1904, **85**, 1323).

Morin.—Morin pentamethyl ether gives, on nitration, *nitromorin pentamethyl ether*, which, on reduction, is converted into the corresponding amino-derivative. As in the case of the analogous quercetin compound, attempts to displace the amino-group by hydroxyl have hitherto failed. *Dibromomorin pentamethyl ether* has been prepared, but from this, by nitration, no appreciable quantity of a nitro-compound could be produced.

Aminomorin hydriodide, from nitromorin pentamethyl ether and hydriodic acid (D 1·7), is soluble in alkalis with a yellowish-brown tint, the additional auxochrome in this case, also, not having caused any noteworthy deepening of colour. Spectroscopic studies which are being carried out by one of us appear to offer an explanation of the difficulty already mentioned (Watson, T., 1914, **105**, 766), namely, that whereas an increase of auxochromes deepens the colour very considerably in certain groups of dyes, as is shown in the difference between alizarin and alizarin-blue, W.R., and fluorescein and gallein, in other cases, such as the flavone group, a similar multiplication of auxochromes has very little effect on the colour.

A multiplication of auxochromes appears to widen the principal absorption band and shift it a little towards the red end of the spectrum, but whereas a slight broadening or shift of a band in the red, yellow, or green part of the spectrum has a great effect on the colour of the substance, the broadening or shifting to an equal extent of a band in the violet, extending from the ultra-violet into the violet end of the spectrum, has very little effect on the visible colour.

Experimental.

Derivatives of Luteolin.

The luteolin tetraethyl ether employed in this investigation was prepared by the method previously described (P., 1912, **28**, 328).

Tetranitroluteolin tetraethyl ether, $C_{15}H_2O_2(OEt)_4(NO_2)_4$, was most readily obtained in a pure condition by slowly adding powdered luteolin tetraethyl ether (1 part) to fuming nitric acid (10 parts) at the ordinary temperature. The clear solution was at once poured into water, the precipitate collected, dried, and crystallised from a mixture of acetic acid and alcohol. The yield of the substance, which consisted of colourless, slender prisms, melting at 196°, was equal to that of the luteolin tetraethyl ether originally employed. This substance could also be obtained by nitrating with equal parts of sulphuric acid and nitric acid (D 1·42 or 1·5) at the ordinary temperature, but the yield was not good. Mixtures of nitric acid and acetic acid at the ordinary temperature and at 60° were experimented with in the hope of preparing a mononitro-compound, but without success. The tetranitro-derivative is sparingly soluble in alcohol, but more readily so in acetic acid.

Found, N = 9·4, 9·4.

$C_{23}H_{22}O_{14}N_4$ requires N = 9·7 per cent.

Bromoluteolin tetraethyl ether perbromide, $C_{15}H_5O_2(OEt)_4Br,HBr_3$.—Two grams of bromine (4 mols.) dissolved in 20 c.c. of acetic acid were added to a solution of luteolin tetraethyl ether (1 gram) in 20 c.c. of acetic acid. The bright, orange-yellow precipitate thus formed became crystalline (slender prisms) on boiling the mixture for a few minutes. After remaining overnight, the perbromide was collected, washed with acetic acid, and dried over soda-lime. It softens at 157°, and melts and decomposes at 161°.

Found, C = 38·5; H = 4·36; Br = 45·0.

$C_{23}H_{26}O_6Br_4$ requires C = 38·4; H = 3·6; Br = 44·5 per cent.

Bromoluteolin tetraethyl ether hydrobromide, $C_{15}H_5O_2(OEt)_4Br,HBr,C_2H_4O_2$, was obtained when luteolin tetraethyl ether in acetic acid solution was treated with 1 molecule of halogen. On boiling the mixture, the precipitate became crystalline, and consisted of hair-like needles of a paler yellow colour than those of the perbromide. The same substance could be obtained by the addition of hydrobromic acid to a glacial acetic acid solution of bromoluteolin tetraethyl ether. For analysis, it was dried over soda-lime.

Found, C=49·2, 48·4; H=5·1, 5·3; Br=25·2, 25·8.

$C_{25}H_{30}O_8Br_2$ requires C=48·5; H=4·9; Br=25·8 per cent.

Bromoluteolin tetraethyl ether, $C_{15}H_5O_2Br(OEt)_4$, was obtained in quantitative yield by boiling the hydrobromide with water. Nine grams were obtained from 10 grams of luteolin tetraethyl ether by this method. It is also the main product of the action of boiling water, alcohol and water, or dilute sulphurous acid on the perbromide described above, and may also be prepared by brominating luteolin tetraethyl ether in acetic acid solution and in the presence of sodium acetate. In these circumstances, however, by-products are formed, and the purification of the material is troublesome. It crystallises from a mixture of alcohol and acetic acid in colourless, hexagonal plates, melting at 183°.

Found, C=57·8; H=5·5; Br=16·9.

$C_{23}H_{25}O_6Br$ requires C=57·8; H=5·3; Br=16·8 per cent.

Tetrabromoluteolin tetraethyl ether, $C_{15}H_2O_2Br_4(OEt)_4,H_2O$, is one of the products of the bromination of luteolin tetraethyl ether with two molecules of halogen in acetic acid solution in the presence of sodium acetate. The slight precipitate of oxonium salt was removed, water added to the filtrate, and the product collected and crystallised from a mixture of alcohol and acetic acid. The first deposit consisted chiefly of the monobromo-compound, whereas the tetrabromo-derivative subsequently separated. A better method of separation consisted in adding hydrobromic acid to an acetic acid solution of the mixture, in which case the monobromo-compound was precipitated as hydrobromide, whereas tetrabromoluteolin tetraethyl ether, which does not yield a hydrobromide, remained in solution, and was subsequently deposited in colourless, lenticular crystals, melting at 111—114°.

Found, C=37·9; H=3·4; Br=43·1.

$C_{23}H_{24}O_7Br_4$ requires C=37·7; H=3·3; Br=43·7 per cent.

Bromo-6′-nitroluteolin tetraethyl ether, $NO_2{\cdot}C_{15}H_4O_2Br(OEt)_4$.—Finely powdered bromoluteolin tetraethyl ether (1 part) was gradually added to nitric acid (D 1·4: 5 parts), which had been previously boiled with carbamide nitrate. Towards the end of the addition, the oxonium nitrate of the unchanged tetraethyl ether separated in bright, yellow needles. The mixture was now heated to 60° for half an hour, and, on cooling, the nitro-compound was deposited as an oil, which quickly changed to large, rhombic crystals. Water was then added, and the precipitate collected and crystallised from a mixture of acetic acid and alcohol. It consisted of pale, cream-coloured rhombs, melting at 170—171°. Thirteen grams of bromoluteolin tetraethyl ether gave 11·4 grams of the nitro-compound.

Found, C=53·0; H=4·6; Br=15·0.

$C_{23}H_{24}O_8NBr$ requires C=52·9; H=4·6; Br=15·3 per cent.

Bromo-6′-aminoluteolin tetraethyl ether.—A mixture of 0·5 gram of the nitro-compound, 12 c.c. of alcohol, 2·5 c.c. of concentrated hydrochloric acid, and 1·25 grams of stannous chloride was gently boiled for a few minutes, causing the development of a deep crimson colour. After a few hours, the product was poured into water acidified with hydrochloric acid, and the crimson precipitate (which consists of the tin double chloride of the base) was collected, well washed, and finally boiled with water, causing it to become yellow, owing to the production of the free base. This was collected, dried, and, by crystallisation from alcohol, was obtained in short, yellow prisms, melting at 165—169°, readily soluble in alcohol or acetic acid. In a second preparation, 11 grams of the nitro-compound gave 7·3 grams of the crystalline base.

Found, C=56·3; H=5·6; Br=15·8.

$C_{23}H_{26}O_6NBr$ requires C=56·1; H=5·3; Br=16·3 per cent.

The *hydrochloride*, $C_{15}H_4O_2Br(OEt)_4{\cdot}NH_2,HCl,H_2O$, separates when a few drops of hydrochloric acid are added to a solution of the base in alcohol or acetic acid. It forms bright yellow needles which, when dried over soda-lime, become scarlet, and melt and decompose at 187°.

Found, C=50·8, 50·7; H=5·7; Br+Cl=21·2, 21·6.

$C_{23}H_{29}O_7NBrCl$ requires C=50·5; H=5·3; Br+Cl=21·1 per cent.

The *stannichloride*, $(C_{23}H_{26}O_6NBr)_4,H_4SnCl_6$, the intermediate product of the preparation of the base, can also be obtained by adding stannous chloride and hydrochloric acid to the alcoholic solution of the latter. Two c.c. of hydrochloric acid and 0·4 gram of stannous chloride were added to a solution of 0·4 gram of the base in 16 c.c. of boiling alcohol. Hot water was cautiously added, and the mixture allowed to cool, when the salt was deposited in stout, crimson prisms, which were collected, washed with alcoholic hydrochloric acid, and dried in a desiccator. It is remarkable that when bromonitroluteolin tetraethyl ether is mixed with a solution of stannous chloride in hydrochloric acid, no crimson colour develops, but the orange-coloured substance so obtained becomes red on treatment with alcohol or water.

Found, Sn=4·8.

$(C_{23}H_{26}O_6NBr)_4,H_4SnCl_6$ requires Sn=5·1 per cent.

The reduction of bromonitroluteolin tetraethyl ether by alcoholic sodium sulphide proceeds in a different manner, the main product of the reaction being a substance melting at 187°, and crystallising from alcohol in cream-coloured needles. This has not yet been further investigated.

Bromo-6′-hydroxyluteolin tetraethyl ether, $C_{15}H_4O_2Br(OEt)_4 \cdot OH$. —Half a gram of the base was treated with 0·7 c.c. of hydrochloric acid (6 mols.) and 8 c.c. of water, the mixture being boiled in order to convert the base completely into hydrochloride, cooled, and then treated with 0·07 gram of sodium nitrite (1 mol.). The amino-hydrochloride almost completely dissolved, and, on agitation, needle-shaped crystals of *bromoluteolin tetraethyl ether diazonium chloride* were deposited. After keeping for a short time, the mixture was added to 250 c.c. of water, and the resulting solution of the diazonium chloride boiled vigorously for fifteen minutes. The clay-coloured precipitate of the bromohydroxy-compound was collected, and could be crystallised from much boiling acetic acid, but as partial acetylation occurred during this process, it was better first to prepare the acetyl compound by means of boiling acetic anhydride and pyridine, and purify this by crystallisation from acetic acid with the aid of animal charcoal. A small quantity of a red-coloured impurity was thus removed, and the acetyl compound was obtained in white needles, melting at 270—272°. Unfortunately, the employment of the charcoal considerably decreased the yield. By avoiding its use, 4 grams of acetyl derivative possessing a faint pink colour, but melting correctly, could be obtained from 5 grams of the bromoamino-compound.

Found, C=55·9, 55·5; H=5·2, 5·3; Br=14·9.

$C_{25}H_{27}O_8Br$ requires C=56·1; H=5·1; Br=14·9 per cent.

By hydrolysing the acetyl derivative, bromohydroxyluteolin tetraethyl ether was obtained in yellow needles, melting at 255°, almost insoluble in alcohol or benzene, but soluble in cold sulphuric acid with a cherry-red coloration.

Bromo-6′-hydroxyluteolin diethyl ether, $C_{15}H_4O_2Br(OH)_3(OEt)_2$. —When bromohydroxyluteolin tetraethyl ether or its acetyl derivative is digested with boiling hydriodic acid (D 1·7), no solution apparently occurs. One gram of the acetyl derivative was boiled with 50 c.c. of hydriodic acid for one hour, and the product poured into dilute sodium hydrogen sulphite solution. A yellow, semi-crystalline solid was thus obtained, which was not completely soluble in aqueous potassium hydroxide. On acetylation in the usual manner with acetic anhydride and pyridine, this yielded a buff-coloured acetyl derivative, which crystallised in uniform needle-shaped crystals, melting at 213°. The product is apparently *bromo-6′-hydroxyluteolin diethyl ether triacetate.*

Found, C=53·0; H=4·8; Br=15·3.

$C_{25}H_{23}O_{10}Br$ requires C=53·3; H=4·1; Br=14·2 per cent.

It appeared probable that the incomplete de-ethylation of the tetraethyl ether arose from its insolubility in boiling hydriodic

acid, and 1 gram of the substance was now treated with a mixture of 50 c.c. of the acid and 25 c.c. of acetic anhydride for two hours. On pouring into water containing a little sodium hydrogen sulphite, a yellow, gelatinous precipitate (0·36 gram), soluble in alkali, was obtained. This, on acetylation, gave an acetyl derivative, crystallising from acetic anhydride in white needles, which began to sinter at 225°, and melted at 250—256°. A second digestion with acetic anhydride and hydriodic acid was without further result. Distinct preparations of the acetyl compound were analysed.

Found, C = 59·4, 59·7, 59·9; H = 4·4, 4·4, 4·4.

$C_{15}H_5O_2(OAc)_5$ requires C = 58·6; H = 3·9 per cent.

As stated in the introduction, these figures were disappointing, and although it suggested itself that this arose from incomplete de-ethylation, on consideration it seemed more likely that the compound was, in reality, hydroxyacetyl-luteolin contaminated with a small amount of some impurity. In the latter case, it was conceivable that, under the drastic treatment employed, an elimination of a hydroxyl group from a portion of the substance had occurred, the second substance in question being thus either luteolin itself or an isomeric tetrahydroxyflavone. Whichever of these suggestions is correct must remain for future decision, for, owing to the exhaustion of the material, attempts to solve the matter by fractional crystallisation processes were out of the question. On hydrolysis in the usual way, the acetyl derivative yielded the free hydroxy-compound as a gelatinous precipitate, which was subsequently obtained in needle-shaped crystals. It dissolved in alkali solutions with a yellowish-brown colour, and was very similar to luteolin itself.

Nitro-3: 4-*diethoxybenzoic acid*, $NO_2 \cdot C_6H_2(OEt)_2 \cdot CO_2H$.—The oxidation of bromo-6′-nitroluteolin tetraethyl ether with permanganate under the conditions found suitable for the oxidation of nitroquercetin pentamethyl ether gave no satisfactory result, but, on the other hand, the use of this reagent in alkaline solution proved successful. Two grams of the substance, obtained in the gelatinous condition by solution in sulphuric acid and precipitation with water, being subsequently well washed, were rubbed into a paste with an aqueous solution containing 5 grams of potassium permanganate and 5 grams of sodium hydroxide. In about a day, the permanganate having disappeared, the manganese oxide was filtered off, and the pale yellow filtrate acidified and extracted with ether. From the ether a yellow, crystalline residue was obtained, which, after two recrystallisations from benzene, separated in colourless needles, melting at 145—148°. The yield was 0·2 gram.

Found, C = 51·7; H = 5·4.

$C_{11}H_{13}O_6N$ requires C = 51·8; H = 5·1 per cent.

It was evidently nitro-3 : 4-diethoxybenzoic acid.

Derivatives of Morin.

Morin pentamethyl ether.—The preparation of this substance was effected by two methods:

(1) The modification of Valiaschko's process, which proved so successful for the preparation of quercetin pentamethyl ether, and is described in the former communication (Watson, *loc. cit.*). The first stage of the process gave mainly morin dimethyl ether, and the second stage had to be repeated before the pentamethyl ether could be obtained in the pure condition. The yield was 25 per cent.

(2) Herzig and Hofmann's method, with slight modification (*Ber.*, 1909, **42**, 155). Five grams of morin (either the yellow or the colourless variety) were dissolved in a 10 per cent. solution of sodium hydroxide (4 mols.) and shaken in an atmosphere of coal-gas with methyl sulphate (4 mols.). This operation was repeated four times, and, after the last two additions, the flask was heated for half an hour on the water-bath. The product was collected, washed, dried, dissolved in 50 c.c. of alcohol, and poured into 500 c.c. of ether. After removal of insoluble matter, the ethereal solution was shaken three times with 5 per cent. potassium hydroxide solution, and then with water. This caused the separation of the pentamethyl ether in white crystals, which were removed with some difficulty from the mixture of ether and water. The yield was 2·3 grams, and no recrystallisation was necessary.

Nitromorin pentamethyl ether, $C_{15}H_4O_2(OMe)_5 \cdot NO_2$.—The nitration of morin pentamethyl ether proved to be a troublesome operation. As oxidation readily occurs if the nitration mixture is allowed to remain, the process must be carried out rapidly, and quantities greater than 0·2 gram should not be employed at one time. The finely powdered substance was added to 2 c.c. of cold nitric acid (D 1·4), previously boiled with carbamide nitrate, and as soon as all had dissolved, the dark, greenish-blue-coloured solution was poured into water. The precipitate, at first grey, soon became ochreous, and was collected, drained on tile, and crystallised from alcohol, from which it was deposited in reddish-brown needles, melting at 223—225°. The yield was approximately 50 per cent.

Found, N = 3·7.

$C_{20}H_{19}O_9N$ requires N = 3·4 per cent.

It is moderately soluble in alcohol, but more readily so in acetone.

Aminomorin pentamethyl ether, $C_{15}H_4O_2(OMe)_5 \cdot NH_2$.—A mixture of 1 gram of nitromorin pentamethyl ether, 30 c.c. of alcohol, 2 grams of powdered tin, and 6 c.c. of hydrochloric acid was heated slowly until the greater portion of the alcohol had been driven off. On cooling, yellow needles of the stannichloride separated, which were collected, and treated in warm aqueous solution with excess of sodium carbonate, whereby a precipitate, consisting chiefly of lenticular crystals, was deposited. The dried product was extracted with about 250 c.c. of alcohol, and, on concentrating the solution, 0·5 gram of aminomorin pentamethyl ether was deposited in almost colourless, hexagonal plates, melting at 204—205°.

Found, C = 61·9; H = 5·8.

$C_{20}H_{21}O_7N$ requires C = 62·0; H = 5·4 per cent.

It is very readily soluble even in cold dilute hydrochloric acid, and this solution, on addition of platinic chloride, gradually deposits the *platinichloride*, $(C_{20}H_{21}O_7N)_2,H_2PtCl_6$, in stout, yellow prisms.

As stated in the introduction, attempts to prepare the corresponding hydroxymorin pentamethyl ether from the amino-compound by the diazotisation method were unsuccessful, and, indeed, no definite product could thus be isolated.

Dibromomorin pentamethyl ether, $C_{15}H_3O_2Br_2(OMe)_5$.—When brominated in acetic acid solution, the behaviour of morin pentamethyl ether is not the same as that of the luteolin compound above described, for with one molecular proportion of bromine no precipitation of oxonium salt occurs. The following method was eventually adopted.

A solution of 2·25 grams of morin pentamethyl ether in 5 c.c. of boiling acetic acid was treated with 2·9 grams of bromine (3 mols.) in 20 per cent. acetic acid solution, causing the separation of a crystalline precipitate, and, after keeping overnight, this was collected, washed with acetic acid, and dried over soda-lime. This product (3·75 grams), at first brick-red, gradually assumed a pale colour, and may be the *dibromopentamethyl ether perbromide*, which thus slowly loses bromine, with the formation of *dibromomorin pentamethyl ether hydrobromide*. Analysis gave C = 36·7; H = 3·5; Br = 50·0 per cent., and these figures agree approximately with those required by the formula $(C_{20}H_{18}O_7Br_2,HBr)_3,Br$.

It was now digested with boiling sodium hydrogen sulphite solution, and the colourless precipitate was collected, dried, and treated with about 25 c.c. of boiling acetic acid. The almost clear liquid, while still hot, deposited rhombic crystals, melting at 254—264°, in amount equal to the morin pentamethyl ether originally taken. This compound, which consists of *dibromomorin penta-*

methyl ether, after several recrystallisations, melted at 263—270°. It is only sparingly soluble in acetic acid or alcohol, more readily so in chloroform, but is not easy to obtain from these solvents in a well-crystallised condition.

Found, C=45·5; H=3·8; Br=29·8.

$C_{20}H_{18}O_7Br_2$ requires C=45·3; H=3·4; Br=30·2 per cent.

A substance melting at 200—205°, probably bromomorin pentamethyl ether, can be isolated by the employment of one molecular proportion of bromine in the presence of acetic acid, and subsequent addition of a little concentrated hydrobromic acid. The bright yellow oxonium hydrobromide thus precipitated is collected, digested with boiling water, and recrystallised from acetic acid and alcohol. The yield, however, was poor, and on this account the substance was not further investigated.

Attempts to nitrate dibromomorin pentamethyl ether under varied conditions gave unsuccessful results.

Aminomorin, $C_{15}H_4O_2(OH)_5{\cdot}NH_2$.—This substance was obtained by digesting nitromorin pentamethyl ether with boiling hydriodic acid (D 1·7) for one hour. The mixture, on cooling slowly, deposited *aminomorin hydriodide*, $C_{15}H_4O_2(OH)_5{\cdot}NH_2,HI,H_2O$, as either spherulites or square platelets, according to the concentration of the solution. For analysis, it was separated from the acid by decantation, drained on tile, and dried in a vacuum desiccator. The product contained a small amount of free iodine, but as this could not be removed by sulphurous acid without partial hydrolysis occurring, it has been allowed for in interpreting the analytical results.

Found, C=37·1; H=3·6; I=31·1, or, deducting free iodine, C=39·0; H=3·7; I=27·4.

$C_{15}H_{11}O_7N,HI,H_2O$ requires C=38·9; H=3·0; I=27·4 per cent.

It possesses a yellowish-brown colour, is not readily soluble in water or dilute acids, but dissolves in aqueous potassium hydroxide to form a brownish-yellow solution. With acetic anhydride and sodium acetate, a colourless acetyl derivative is produced; this is readily soluble in acetic acid, but, like the acetylation product of morin itself, has not been obtained in a crystalline condition.

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[*Received*, *Jan.* 11*th*, 1915.]

XXII.—*The Wet Oxidation of Metals. Part III. The Corrosion of Lead.*

By Bertram Lambert and Herbert Edwin Cullis.

The numerous researches which have been published on the action of water and oxygen on metallic lead have all been carried out with metal covered with a surface film of oxide.

It is well known that metallic lead, on exposure to the air, undergoes surface oxidation with the production of a dark-coloured oxide, which is generally described as a suboxide. Even the most highly purified lead undergoes this surface oxidation on exposure to the air, although in the case of lead which has been distilled in a vacuum and kept for a long time before exposure to the air, the brilliant metallic lustre is not appreciably dimmed for many days (see later).

The aim of the authors in the present investigation was to study the action of (*a*) water alone, (*b*) water and oxygen together, on metallic lead, first pure water and then pure oxygen being brought into contact with pure metallic lead, under such conditions that the lead, previous to the contact of the water, was entirely free from any trace of oxide.

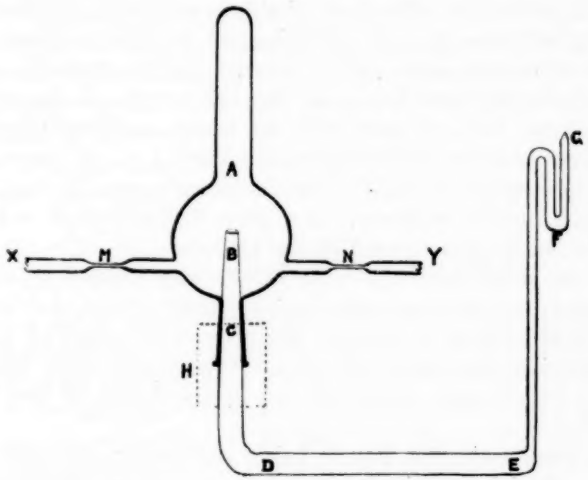
This object was attained by distilling lead (previously made by Stas' method and fractionated in a vacuum) in a quartz apparatus, in a high vacuum, then distilling pure water on to the metal, and finally allowing pure oxygen to come in contact with the lead and water.

The apparatus used for preparing and storing the oxygen, for preparing the water, and for bringing each of them into contact with the metal was identical in every respect with that used in similar experiments on the corrosion of iron (Lambert, T., 1912, **101**, 2058 *et seq.*).*

* In a criticism of these experiments, Armstrong (*Science Progress*, 1913, **8**, 73) insists that, in spite of the elaborate precautions taken, it is impossible, in an apparatus of this kind, to get rid of the gases (especially carbon dioxide) condensed on the surface of the glass. He takes exception to the statement that the whole of the glass surfaces was strongly heated for long periods (during the frequent successive operations of exhaustion which followed the washing out of the apparatus with pure oxygen), and states, in particular, that the large Schmidt stopcocks used in the apparatus could not, in his opinion, have been heated.

The barrels of these stopcocks are made of Jena normal glass and are hollow, the bore consisting of a tube fused across the hollow barrel. Thus the mercury-seal, which covers the top and bottom of the barrel, fills the hollow space in the barrel itself and circulates round the tube, forming the bore of the stopcock. The difference between the coefficients of expansion of the Jena glass of the barrel and

The only difference was in the type of vessel used for the reaction. This was constructed as follows: The vessel *A*, of about 150 c.c. capacity, was made of ordinary soft glass; the side-tubes *M* and *N* were drawn out to capillaries, and were sealed at *X* and *Y* to the oxygen and water supplies respectively. At *C* junction was made between this glass part and the quartz part of the apparatus *BCDEFG* by means of a ground joint. This ground joint was about 4 cm. long, and was ground very accurately. It was lubricated with glacial phosphoric acid, and was protected by a mercury cup *H* (represented in the figure by a dotted line). The quartz part of the apparatus (drawn in fine line in the figure in order to distinguish it from the glass part, which is drawn in thicker line) was of



the shape shown, and was made from transparent quartz tubing. It projected at *B* into the interior of the vessel *A*, so that when water was distilled into it the water which collected there must have condensed on a quartz surface, and could not have been in contact with a glass surface after condensation.

Metallic lead, which had been prepared as described below, was placed in the quartz tube at *F*; it was introduced through the open end *G*, which was then sealed off in the oxy-coal-gas flame.

The whole apparatus between the oxygen storage vessel and the

the ordinary soft glass of the outside makes it possible to heat these stopcocks to 200° without any risk of fracture if the operation is carried out with care. In the experiments the stopcocks were strongly heated to a temperature above 200° by surrounding them with boxes made of asbestos sheeting—so as to give, in effect, a hot air-bath—and then heating the boxes with a Bunsen burner.

water storage vessel (see Fig. 1, T., 1912, **101**, 2058) was then very thoroughly exhausted by means of a mercury pump, and all the glass and quartz surfaces were strongly heated until the Plücker tube attached to the apparatus would not allow any discharge to pass from a large induction coil. The apparatus was then washed out with pure oxygen and exhausted many times, being strongly heated during each process of exhaustion. The residual gases at the end of several of the later operations were frozen out in tubes surrounded with liquid air and examined spectroscopically, but no trace of the carbon dioxide spectrum was ever detected.

The lead was then distilled in the high vacuum thus obtained by surrounding the quartz part of the apparatus *GFE* from *G* almost to *E* with an electrical resistance furnace and raising the temperature to about 1200°. The lead distilled, the oxide on the surface combining with the quartz, and being left behind as a lead silicate together with some metal at *F*. A large globule of metal collected at *E* and smaller globules along the lower part of the tube *EF*. These globules were of very brilliant lustre, and resembled silver or mercury globules in appearance. They had no trace of the bluish colour which is usually associated with metallic lead. Some of the lead vapour condensed as a grey, finely-divided, mirror-like deposit in the neighbourhood of the globules.

After the distillation the quartz tube was allowed to cool, and then water was distilled into the apparatus from a solution of barium hydroxide in a vacuum; the water was caused to collect in *DE* by cooling this part with ice. Oxygen was then allowed to enter the vessel, and afterwards the capillaries at *M* and *N* were sealed off.

It was possible in this way to bring pure water and pure oxygen into contact with pure lead without the previous contamination of the metal with a film of oxide.

For details of the methods of preparing, storing, and testing the purity of the water and oxygen, and for fuller details of the methods employed for bringing them in the highest state of purity into the reaction vessel, see T., 1912, **101**, 2058 *et seq.*

Preparation of the Lead.

Many methods were employed to prepare lead in a high state of purity previous to its distillation in the manner described above, but it was found very difficult to remove all traces of iron. Finally, lead was prepared by the method described by Stas (*Bull. Acad. roy. Belg.*, 1860, **10**, 295). It was cut into small chips by means

of a pure iridium spatula on to which a cutting-edge had been ground.*

The lead was then distilled in clear quartz tubes, which were about 7—8 mm. bore and 25 cm. long, and were divided into three compartments by narrowing the tube down to capillaries. The tubes were exhausted while the metal was kept in the molten state, and finally the lead was distilled at about 1200°. The first fraction was collected in the first compartment, which was then sealed off. The middle fraction was collected in the second compartment, whilst the residue was left behind in the third compartment. It is worthy of note that the globules of lead obtained in this way adhered very closely on the under side to the quartz, producing a very fine reflecting surface. It was found that if the distilled lead was exposed to air a short time after distillation, but when quite cold, the brilliant surface was quickly dimmed by a film of oxide. If, however, the metal was kept in the vacuous tube for several months, exposure to the air did not then cause any appreciable decrease in its brilliant lustre for several days.

It was only the middle fraction of lead that was used in the experiments described above.

Results of Experiments and Discussion.

In all the earlier experiments the water and oxygen were brought into contact with the lead within a few days of the distillation, and the results were the same. Very rapid oxidation took place. In the case of the metal, which was under the surface of the water, this resulted in the formation of crystals of white lead hydroxide, together with a brown-coloured oxide or hydrated oxide. The white crystals were detached from the metal, and at first caused a kind of opalescence in the water; the brown-coloured oxide adhered to the surface of the metal. The opalescence was visible within a few hours of the admission of the oxygen. The small globules of metal which were out of contact with the liquid water behaved similarly; the metallic lustre disappeared quickly, and a dark brown (almost black) coating of oxide appeared on the surface of the lead.

In the case of the grey films of metal which were not under the surface of the water the result was very striking; within half an hour after the admission of oxygen the grey films turned bright yellow throughout, and then after a few days the yellow colour began to change to a dull red. This latter change was slow, and

* Pure iridium is so hard that it is possible to grind a sharp cutting-edge on to a plate of the metal.

requires many months for completion. It is accelerated by light.*

The yellow substance is undoubtedly the unstable, yellow form of lead oxide, which is then gradually converted into the more stable red modification. It affords an interesting example of Ostwald's law of successive reactions.

It would appear from these experiments that metallic lead, even when very pure, undergoes very rapid oxidation in contact with pure water and pure oxygen.

It seemed possible, however, that lead which was freshly distilled in this way, in spite of its chemical purity, might not be physically homogeneous. In all probability metallic lead can exist in more than one physically different form, and in the change from the vapour phase (through the liquid) to the solid phase, the most unstable form would be produced at first. Judging from analogy to similar cases, one would expect that the change (or changes) from the unstable form (or forms) to the stable form would be slow, and so a globule of lead prepared by distillation would, soon after its preparation, contain more than one modification of the metal.

According to the electrolytic theory of corrosion, as interpreted by one of us (*Trans., Faraday Soc.*, 1913, **9**, 108), the lead, being physically heterogeneous, would tend to pass into solution in the electrolyte water because the different modifications of the metal, having different electrical potentials (or solution pressures), would tend to produce an electric current, with the consequent passing into solution of the metal at the relatively electropositive parts.

Now pure metallic lead is insoluble in water, in a vacuum, so far as chemical tests show. This was proved by experiments carried out in a similar manner to the above, in which freshly distilled lead was brought into contact with pure water in a vacuum, and left for many months; the water was then removed, evaporated down to a small bulk, and subjected to careful tests, but no positive evidence was ever obtained of the presence of lead in solution. This can only be taken to show, however, that the rate at which chemically pure, but physically heterogeneous, lead passes into solution in pure water is infinitesimally small, or so small that insufficient lead passes into solution, even after long periods of time, to be detected by chemical tests.

Corrosion is, however, undoubtedly preceded by, and takes place

* Ordinary litharge, which consists of a mixture of these two forms of lead oxide and, when freshly obtained, is yellowish, turns darker in colour when exposed to the action of light.

through, a process of solution of the metal, so that the rate at which lead passes into solution in water must be enormously increased by the presence of oxygen. It seems probable that the case is parallel with that of iron; oxygen probably accelerates the passing of the lead into solution by destroying the polarisation, which, in the absence of oxygen, is sufficient to reduce to an infinitesimal value the electric current which can pass between the electrically different parts of the metal.

If these considerations are valid, then pure metallic lead, if it be kept in a vacuum a sufficiently long time for the unstable forms to change into the stable form—for the metal to become physically as well as chemically homogeneous—might be expected to withstand the action of water and oxygen without undergoing corrosion.

In order to test this possibility, two exactly parallel experiments were carried out, side by side, in two vessels of the type described above. The lead used in each case was from the same fraction, and the temperature at which the lead was subsequently distilled, in the two vessels, was the same. Within twenty-four hours after the distillation of the lead, water was distilled into the two vessels, and then one of the vessels, containing pure lead and pure water only, in a vacuum, was sealed off and set aside for twelve months. Oxygen was admitted into the other vessel before it was sealed off, and the result in this case was the same as that described above.

After the lead in the first vessel had remained in contact with water in a vacuum for twelve months the metallic lustre of the metal was quite unaffected. The point of one of the capillaries was then broken off in an atmosphere of pure oxygen, and the gas thus allowed to come into contact with the lead and water. For more than a week there was no visible tarnishing of the brilliant metallic surface of the large globule of lead which was under the surface of the water, but after that time the metallic lustre was gradually dimmed by the formation of a dark-coloured coating of oxide on its surface. The rate of corrosion was, however, so slow that after more than six months' exposure to the combined action of water and oxygen the layer of oxide was thin enough to display interference colours. After exposure for nearly a year the globule of lead is covered with a layer of a dark brown oxide, and minute crystals of hydrated lead oxide can be seen in the water.

The surface of the smaller globules of lead along the portion of the tube *EF* and out of contact with liquid water was oxidised very slowly. but, perhaps most striking of all, the grey films of finely-divided lead which underwent such rapid oxidation in the parallel experiment showed no similar change; for many months there was no apparent change in their appearance, but now, after

nearly a year, a small patch of the yellow form of the oxide has appeared.

The differences between the behaviour of the lead in these two parallel experiments is very striking and significant. Although keeping the pure lead for a period of one year in water in a vacuum does not result in entirely preventing corrosion when oxygen is brought into contact with the metal, yet the rate of the oxidation is enormously decreased.

The differences between the two specimens of lead, prepared in precisely the same manner—differences brought out by "ageing" the metal—are probably only differences of a physical character. If, as seems probable, lead can exist in different modifications, the more unstable forms will predominate in the freshly distilled metal, and thus give it a heterogeneous character, which is, moreover, gradually changing. When the metal is kept for a long time in a vacuum it would become more homogeneous as far as its physical character is concerned, and consequently the rate at which it would pass into solution in water in the presence of oxygen would be greatly decreased.

The results of these experiments thus afford very strong evidence of the validity of the electrolytic theory of corrosion.

In the corrosion of lead, the metal probably passes into solution as lead ions, owing to the electrolytic action between the electrically different parts of the metal. In the absence of oxygen, the velocity of this action is infinitely small, because the hydrogen separating out at the relatively electronegative parts introduces an enormous resistance to the passage of the current. Oxygen greatly accelerates the action by oxidising the film of hydrogen—destroying the polarisation—producing water and, probably, hydrogen peroxide (see later).

The lead ions then combine with the hydroxyl ions of the water to form an undissociated lead hydroxide, since lead is a very weakly basic element.

If, as seems probable, the dark-coloured oxide first formed on the metal is a hydrated, plumbous oxide, $Pb_2O,2H_2O$, the lead will pass into solution as plumbous ions and produce, with the hydroxyl ions, an undissociated plumbous hydroxide. In that case, the oxygen will play a second part, in oxidising the plumbous to plumbic hydroxide—the ordinary white, crystalline hydroxide of lead.

It has been shown by Traube (*Zeitsch. physikal. Chem.*, 1900, **32**, 137), Dunstan (T., 1911, **100**, 1835) and others, that hydrogen peroxide is formed when lead, water, and oxygen are brought together. The hydrogen peroxide theory of the corrosion of metals

was first put forward by Traube, and, according to this theory, the reactions involved in the wet oxidation of lead were represented thus:

(1) $Pb + H_2O + O_2 = PbO + H_2O_2$.
(2) $PbO + H_2O = Pb(OH)_2$.
(3) $Pb + H_2O_2 = Pb(OH)_2$.

Now, Traube has shown that hydrogen peroxide is formed when oxygen is passed through the cathodic chamber of an electrolytic cell in which dilute sulphuric acid is being electrolysed between platinum electrodes. The hydrogen peroxide must be formed by the action of ordinary molecular oxygen on electrolytically-formed hydrogen, probably at the moment of its formation, and while it is in the nascent state.

Since lead passes into solution in water, by a process of electrolysis involving the formation of hydrogen, one would expect some hydrogen peroxide to be formed as well as water, but the formation of this substance is not directly concerned with the wet oxidation of lead or any other metal.

It might be expected, however, that the hydrogen peroxide would have a further oxidising action on the lead oxide produced, and this proves to be the case. It was stated above that the film of finely divided lead, produced by distilling the metal, underwent very rapid and complete oxidation, with the production, first, of the yellow modification of lead monoxide, and then of the more stable red form. This oxide film (both the yellow and red forms) is very readily soluble in cold dilute nitric acid if treated with the acid within a few days of its production. If the action is allowed to go on, as it was in some cases, for many months, then the oxide film is not completely soluble in dilute nitric acid, but leaves behind a brown deposit of lead peroxide, PbO_2. The examination of some specimens of lead that had been in contact with water and oxygen for many years showed quite appreciable amounts of higher oxides, which gave the brown peroxide when treated with dilute nitric acid.

Either or both of the oxides, Pb_2O_3, Pb_3O_4, might be present (a quantitative analysis was not possible), and they are probably formed by the action of hydrogen peroxide on the lower oxide.

Summary of Conclusions.

(1) Pure lead which has been distilled in a vacuum undergoes very rapid corrosion when subjected to the action of pure water and pure oxygen within a short time of the distillation of the metal. Chemical tests fail to show the presence of lead in solution before the addition of oxygen.

(2) If the lead prepared in this way is kept for long periods in water, in a vacuum, before the oxygen is added, the rate of corrosion is enormously decreased.

(3) Pure lead which has been distilled in a vacuum, and kept for some months, can be exposed to ordinary air for many days without any appreciable diminution of its brilliant metallic lustre, but more prolonged exposure causes the gradual formation of a dark-coloured oxide on the surface of the metal. The pure, distilled lead resembles silver or mercury in appearance, and shows none of the blue or bluish-grey colour usually associated with metallic lead.

(4) The electrolytic theory of corrosion is applicable to lead. The passing of the metal into solution, which precedes corrosion, is due to electrolytic action between the electrically different parts of the mass of lead. In the case of chemically pure lead, the physical heterogeneity (due to the presence of different allotropic modifications of lead in the mass of metal) causes parts of the mass to be electrically different from other parts, and these electrical differences persist for a long time after the preparation of the metal.

(5) Hydrogen peroxide, which is produced in the wet oxidation of lead, is the product of a subsidiary action, and has no direct bearing on the process of corrosion. It plays a part, however, in oxidising the monoxide to higher oxides.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD. [*Received, Dec.* 18*th*, 1914.]

XXIII.—*The Wet Oxidation of Metals. Part IV. The Question of Passivity.*

By BERTRAM LAMBERT.

THE study of the properties of pure iron throws some light on the question of the cause of the passivity of metals.

It may be said that pure iron possesses to a much more marked extent and in a much more permanent form, the properties which are held to distinguish passive iron.

Passive iron can be kept in contact with very dilute solutions of copper sulphate for short periods without causing the deposition of copper on the iron, but the iron very soon regains its active state, and, if the solution of copper sulphate is of greater concentration than 1 per cent., the passivity seems to be destroyed at once; pure iron can be kept, at the ordinary temperature, for appa-

rently indefinite periods in solutions of copper sulphate without causing copper to be deposited on the iron and solutions of any concentration may be used.

Passive iron can be kept in pure water, in the presence of oxygen, without undergoing corrosion, as shown by Moody and by Friend, but if ordinary air is substituted for oxygen, the small quantity of carbon dioxide contained in the air quickly destroys the passivity, and corrosion takes place; pure iron can be kept in water in the presence of oxygen, ordinary air, or oxygen containing as much as 20 per cent. of carbon dioxide, without showing any signs of corrosion even after several years.

The deposition of copper from copper salt solutions by metallic iron and the rusting of the metal are both preceded by and are a consequence of the metal passing into a state of solution. The fact that these two reactions, which take place readily with all commercial forms of iron, are retarded or inhibited by making the same iron passive, shows that the tendency of passive iron to dissolve in an electrolyte is much less than that of ordinary active iron. The tendency of pure iron to pass into solution in an electrolyte is, of course, still less.

There seems to be very little doubt that the passing of the metal into a state of solution is an electrolytic action. It has been suggested (T_2 1912, **101**, 2068) that pure iron owes its peculiar properties to the physical homogeneity of its surface, and it seems reasonable to argue that passive iron has, in a much less permanent form, a similar homogeneity of surface.

Ordinary commercial iron can be made passive by many widely-differing processes, and it is very improbable that the actual cause of the passivity can be the same in all cases. It may be said with reasonable certainly, however, that the passivity is always due to the formation of a complete and unbroken protective layer of some kind or other. So long as the passivity lasts the iron is in an electrically equable state—it possesses little or no tendency to pass into solution in an electrolyte. The disruption of this protective surface-layer, whatever be its nature, by a slight scratch, makes the iron active again, and the activity always first shows itself at the place where the protective layer has been broken.

The criticism has been made (Armstrong, *Science Progress*, 1913, **8**, 82), in spite of the experimental evidence to the contrary, that the author's pure iron may owe its peculiar properties to a thin protective surface-layer of oxide.

It has been pointed out that when the pure iron is subjected to strong pressure (scratching is not sufficient) it loses its peculiar properties, and (*a*) undergoes corrosion in contact with water and

oxygen, (*b*) causes the deposition of copper from solutions of copper sulphate. Unlike passive iron which has been pressed (or bruised in any way), the rusting always takes place at those parts of the metal which have *not* been pressed, the pressed or bruised part remaining quite bright in contact with water and oxygen for very long periods. It is clear, then, that the iron first shows its activity, and passes into solution at the unbruised part. This is amply confirmed by its behaviour towards copper salt solutions, and also towards the ferroxyl reagent. In the former case copper is always first deposited on the unpressed part, and in the latter case Turnbull's blue appears only at the unpressed portions of the metal.

It seems very unlikely, in the face of these experimental facts, that the peculiar properties of the iron are due to a protective layer of oxide, for, if such were the case, one would expect the bruised metal to show its activity at the parts where the protective layer had been broken in the same way as it does when a piece of commercial iron, made passive by any of the usual methods, is scratched or bruised. It is much more likely, as suggested earlier, that the inactivity of the pure iron is due to its having a physically homogeneous surface consisting of one form of the metal. The effect of strong pressure would be to disturb the physical homogeneity of the surface—to produce, at the part under strain, a modification of the metal which is electrically different from the rest of the mass —and destroy the electrically equable surface.

Armstrong (*loc. cit.*) thinks that two parts of a metal plate, chemically the same but physically different, would not be at different potentials. The experiments of Cohen (*Zeitsch. physikal. Chem.*, 1899, **30**, 613) and others (Spring, *Bull. Acad. roy. Belg.*, 1903, **12**, 1033, etc.) have proved beyond any doubt that alterations in the physical condition of a metal have a marked effect on its potential, and it has been shown that a measurable electric current can be produced from a voltaic cell in which the poles consist of two sheets of the same metal, one of which has been subjected to a strain.

In the case of ordinary commercial iron the presence of chemical impurities—chemical heterogeneity—makes it impossible to have a physically homogeneous surface, and, in consequence, there must always be a tendency for such a metal to pass into solution in an electrolyte. Such iron must always be active in character; it must always corrode in contact with water, if oxygen is present, and it must always deposit copper from solutions of copper salts, even in a vacuum, since in this case polarisation cannot influence the rate of solution of the metal.

When the metal is made passive, the passivity is confined to a

very thin surface layer, which very easily undergoes disruption. Whatever be the chemical nature of the layer—and it is very probable that it is not always of the same chemical nature—the tendency for the metal to pass into solution at this surface, in an electrolyte, is enormously reduced; the surface of the metal has been rendered electrically equable.

Passivity, then, may be defined as the production, by some chemical or electrochemical process, of a physically homogeneous layer on the surface of a metal of which the surface was originally physically heterogeneous.

The author's pure iron is passive in this wide sense; it has a physically homogeneous, and consequently electrically equable surface, the surface in this case being undoubtedly metallic iron.

Some of the methods of making commercial iron passive may possibly result, as Moody claims, in cleansing the surface of the metal from impurities, and giving, in effect, a surface of pure iron, but there is no sound evidence in favour of this hypothesis, and it seems, on the face of it, to be very unlikely.

In the case of a metal like iron, which is known to exist in many physically different modifications, we should not expect that chemical purity would, of necessity, lead to physical homogeneity, and this is borne out by practical experience.

In the preparation of pure iron by the author's method, the same sample of ferric nitrate, treated in exactly the same manner throughout its conversion into iron, will not always give like specimens of the metal. Some of the iron will remain in contact with water, exposed to air for an indefinite time without undergoing corrosion, whilst other specimens will undergo corrosion in a few hours. Similar differences are shown in the behaviour of the metal towards solutions of copper sulphate or copper nitrate. Those pieces of iron which do not undergo corrosion are not affected by solutions of the sulphate or nitrate of copper, and the converse is also true. This is what would be expected according to the theory.

The differences in these pieces of iron must be physical and not chemical in character. The only variable factors in the preparation are the temperature of the reduction of the oxide and the rate of cooling, both of which are very difficult to control at all accurately under the conditions of the experiment.

As a general rule, all the pieces of one batch of iron behave exactly alike, but, in the same batch of specimens of iron made by one and the same reduction, it is sometimes possible to find pieces of metal of both kinds. In a "bad" batch, however, it is only the very small pieces of metal which are satisfactory.

The larger pieces would naturally be affected most by any slight

fluctuations in the conditions which are necessary to produce exclusively one modification of the metal; the possibility of the formation, and continued existence, of other (unstable) allotropic forms would be greater in the case of the larger pieces.

The validity of the above arguments finds strong support in the following facts, which are based on long series of experiments: A very large proportion of the pieces of iron in a "bad" batch can be made to lose their active character and assume the property of non-corrodibility by being kept for several months either in dry air or in a vacuum. The same effect is also produced by re-heating the pieces of metal for a long time at about 1000°, either to a current of pure dry hydrogen or in a high vacuum, hydrogen being given off in considerable quantities in this last operation.

When all the experimental evidence is considered, it is very difficult to explain the inactivity of the author's pure iron except on the assumption that it has a physically homogeneous, and so electrically equable, surface of metallic iron, and consequently it possesses no tendency to pass into solution in an electrolyte.

The results of experiments on the corrosion of pure lead (see preceding paper) add considerable weight to the above considerations.

UNIVERSITY CHEMICAL LABORATORIES,
OXFORD.

[*Received, Dec. 18th*, 1914.]

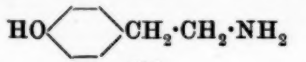
XXIV.—*The Synthesis of* p-*Thiol-β-phenylethylamine.*

By HAROLD KING.

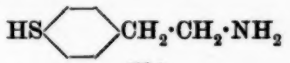
IT is well known that many of the amines derived, through loss of carbon dioxide, by putrefactive processes from the amino-acids occurring in proteins, possess marked physiological activity. Their action, in that they produce effects simulating those caused by stimulation of the sympathetic nervous system, has been termed sympathomimetic (Barger and Dale, *J. Physiol.*, 1910, **41**, 21), and one of the most marked of sympathomimetic actions is the transitory rise of blood-pressure produced on intravenous injection. Three of these putrefactive bases, namely, β-amino-4-ethylglyoxaline from histidine, *p*-hydroxy-β-phenylethylamine from tyrosine, and β-phenylethylamine from phenylalanine, have received valuable therapeutic application.

The search for new bases of a similar type has led to the synthesis of a host of new compounds, a few only of which have been recommended as substitutes for the natural active principles.

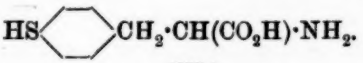
In the course of some synthetic experiments bearing on the above subject, it was thought desirable to investigate the effect on the activity of replacing the hydroxyl group in *p*-hydroxy-β-phenylethylamine (I) by the thiol group. There would thus be produced *p*-thiol-β-phenylethylamine (II), the product of decarboxylation of *p*-thioltyrosine (III), an amino-acid, which, so far, has not been found in nature, but has been synthesised by Johnson and Brautlecht (*J. Biol. Chem.*, 1912, **12**, 175):



(I.)



(II.)



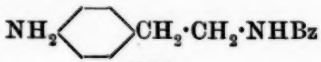
(III.)

The synthesis of the *p*-thiol base (II) might be accomplished in various ways.

First, thioltyrosine (III) might reasonably be expected to furnish the required base by loss of carbon dioxide, inasmuch as tyrosine, when heated under favourable conditions, can give a 50 per cent. yield of *p*-hydroxy-β-phenylethylamine (I), and, moreover, Johnson and Brautlecht state that thioltyrosine melts at about 250°, and the melting is accompanied by effervescence. The synthesis of thioltyrosine being a long process, this method was not put to the test.

Secondly, the direct replacement of the hydroxyl group in *p*-hydroxy-β-phenylethylamine (I) by the thiol group might be effected by means of phosphorus pentasulphide. This was tried, but although both substances are soluble in boiling xylene, the hydroxy-compound was recovered, for the most part, unchanged.

Thirdly, the synthesis might be accomplished using as a starting point benzo-*p*-amino-β-phenylethylamide (IV):

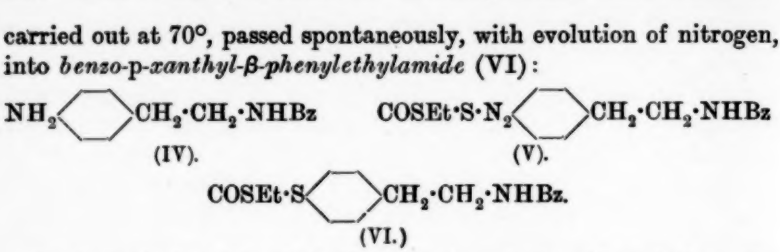


(IV.)

which was employed by Barger and Walpole (T., 1909, **95**, 1722) in one of their syntheses of *p*-hydroxy-β-phenylethylamine. This, indeed, proved to be a suitable foundation, from which the desired synthesis was effected without much difficulty.

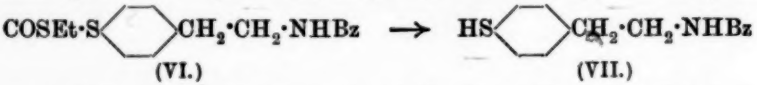
Benzo-*p*-amino-β-phenylethylamide (IV) was diazotised, and converted, by Leuckardt's method (*J. pr. Chem*, 1890, [ii], **41**, 179) by the action of potassium xanthate in alkaline solution, into benzo-*p*-xanthyldiazo-β-phenylethylamide (V). The latter was not isolated, but under the conditions of the experiment, which was

carried out at 70°, passed spontaneously, with evolution of nitrogen, into *benzo*-p-*xanthyl*-β-*phenylethylamide* (VI):



(IV). (V). (VI.)

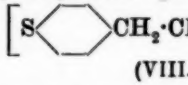
On hydrolysis with alcoholic potassium hydroxide solution, the latter gave *benzo*-p-*thiol*-β-*phenylethylamide* (VII) in a yield



(VI.) (VII.)

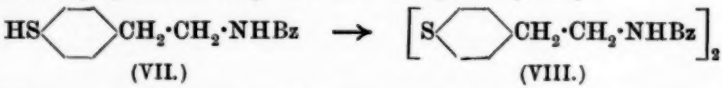
corresponding with 73 per cent. of the theoretical, calculated on the *p*-amino-compound (IV) used.

Benzo-*p*-thiol-β-phenylethylamide (VII) proved to be very susceptible to oxidising agents, mere contact with the atmosphere or crystallisation from organic solvents leading to partial formation of *dibenzodi*-β-*phenylethylamide* p-*disulphide* (VIII),



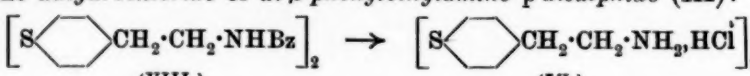
(VIII.)

As a consequence, when the *p*-thiol compound (VII) was subjected to acid hydrolysis, the product was found to be impure. To obviate this difficulty, the *p*-thiol compound (VII) was converted, by oxidation in alkaline solution with potassium ferricyanide, practically quantitatively into the disulphide (VIII):



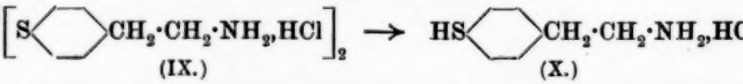
(VII.) (VIII.)

The latter compound was hydrolysed under pressure with 20 per cent. hydrochloric acid at 150°, and gave an 87 per cent. yield of the *dihydrochloride* of *di*-β-*phenylethylamine* p-*disulphide* (IX):



(VIII.) (IX.)

On reduction with tin and hydrochloric acid in the presence of alcohol, the last-named compound gave a 72 per cent. yield of the *hydrochloride* of p-*thiol*-β-*phenylethylamine* (X):



(IX.) (X.)

All the thiol compounds and disulphides obtained in this investigation give the colour reaction described by Johnson and

Brautlecht for thioltyrosine and its disulphide. When dropped into sulphuric acid at 200°, a beautiful purple colour is produced. Unlike tyrosine and *p*-hydroxyphenylethylamine, the characteristic reaction with Mörner's reagent was not obtainable with *p*-thiol-β-phenylethylamine or any of its derivatives.

The physiological action of *p*-thiol-β-phenylethylamine and its oxidation product, di-β-phenylethylamine *p*-disulphide, was investigated by Mr. J. H. Burn, of the Wellcome Physiological Research Laboratories, to whom the author wishes to express his thanks. Their power to produce transitory rises of blood-pressure when injected intravenously into a pithed cat were compared with the similar action of *p*-hydroxy-β-phenylethylamine. *p*-Thiol-β-phenylethylamine had about one-sixth the pressor activity, and the disulphide one-thirtieth the activity, of *p*-hydroxy-β-phenylethylamine.

EXPERIMENTAL.

*Preparation of Benzo-*p*-amino-β-phenylethylamide* (IV).

Thirty-six grams of benzo-*p*-nitro-β-phenylethylamide, prepared by the nitration of benzo-β-phenylethylamide, which is itself most readily obtained by v. Braun's shortened process (*Ber.*, 1911, **44**, 2870), were suspended in 270 c.c. of absolute alcohol, and 29 grams of tin foil added. To the mixture, 135 c.c. of concentrated hydrochloric acid were added, with external cooling (compare Barger and Walpole, *loc. cit.*), and the contents boiled under a reflux condenser for two hours. The solution, decanted from the remaining tin and diluted with its own volume of water, was freed from alcohol by concentration under diminished pressure. The residual aqueous liquor was made alkaline with 10 per cent. aqueous sodium hydroxide solution, and the precipitated tin hydroxides dissolved by the addition of 50 per cent. aqueous sodium hydroxide solution.

The insoluble base was then extracted by means of chloroform, being only very sparingly soluble in ether. The chloroform extract was evaporated to dryness, when it readily crystallised. The yield of crude base, melting at 128—130°, was 31 grams, and on recrystallisation from ethyl acetate 28·5 grams of pure base were obtained. The yield was 90 per cent. of the theoretical. (Found, C=74·9; H=6·9. Calc., C=74·9; H=6·7 per cent.)

Benzo-*p*-amino-β-phenylethylamide crystallises from four and a-half times its weight of ethyl acetate in colourless, massive columns or tablets, which melt at 132—133° (133·5—134·5° corr.) (Barger and Walpole give 134°). It is readily soluble in chloroform or acetone, boiling ethyl acetate, ethyl alcohol or methyl alcohol, but sparingly so in the cold. In hot benzene or xylene it is very sparingly soluble.

The hydrochloride crystallises in the anhydrous condition from ten times its weight of boiling water, to which a small amount of hydrochloric acid has been added, in colourless, glistening hexagonal leaflets. It melts and decomposes at 279—281° (283—285° corr.); Barger and Walpole describe the hydrochloride as melting and decomposing above 280°. (Found, C = 65·2; H = 6·3; Cl = 12·5. Calc., C = 65·1; H = 6·2; Cl = 12·8 per cent.)

The *sulphate* crystallises from water in colourless, glistening six-sided leaflets, which melt and decompose at 273—274° (278—279° corr.), with sintering at 263°. It is very sparingly soluble in water, dissolving to the extent of 1 per cent. at 100°:

0·1408 gave 0·3226 CO_2 and 0·0756 H_2O. C = 62·5; H = 6·0.

0·4034 „ 0·1638 $BaSO_4$. S = 5·6.

$(C_{15}H_{16}ON_2)_2,H_2SO_4$ requires S = 5·5; C = 62·2; H = 5·9 per cent.

The *acetyl* derivative is soluble in twelve times its weight of boiling 95 per cent. alcohol, and crystallises in delicate, rectangular leaflets. It melts at 206—207° (209·5—210·5° corr.):

0·1528 gave 0·4039 CO_2 and 0·0885 H_2O. C = 72·1; H = 6·4.

$C_{17}H_{18}O_2N_2$ requires C = 72·3; H = 6·4 per cent.

Benzo-p-*xanthyl*-β-*phenylethylamide* (VI).

Twenty-four grams of finely powdered benzo-*p*-amino-β-phenylethylamide were suspended in 150 c.c. of 10 per cent. aqueous hydrochloric acid. The mixture, cooled to 0°, was diazotised by the gradual addition of 8·5 grams of sodium nitrite in 30 c.c. of water. The faintly coloured solution, filtered from a little undissolved solid, was run, over the space of half an hour, into a rapidly stirred solution of 32 grams of potassium xanthate dissolved in 130 c.c. of 10 per cent. aqueous sodium carbonate. The latter solution was kept at a temperature of about 70° throughout the experiment. As the diazonium solution dropped into the xanthate solution, benzo-*p*-xanthyldiazo-β-phenylethylamide separated as a bright yellow cloud, but rapidly collected at the surface as an oil, with simultaneous evolution of nitrogen, thus passing into benzo-*p*-xanthyl-β-phenylethylamide. When all the diazonium solution had been added, the stirring was continued for a further fifteen minutes to complete the decomposition. On cooling, the pale brown oil rapidly solidified in large lumps, which were collected, and submitted to the next process of hydrolysis without further purification.

*Hydrolysis of Benzo-*p*-xanthyl-β-phenylethylamide. Formation of Benzo-*p*-thiol-β-phenylethylamide* (VII).

The crude benzo-*p*-xanthyl-β-phenylethylamide was dissolved in 200 c.c. of warm absolute alcohol, 25 c.c. of 50 per cent. aqueous potassium hydroxide solution were added, and the dark reddish-brown solution was boiled for forty-five minutes on the water-bath. Charcoal was now added, and the boiling continued for a further fifteen minutes. The filtered solution, after addition of 300 c.c. of water, was freed from alcohol by concentration under diminished pressure. When cold, 3·7 grams of insoluble solid, *A* (p. 228), were collected. The filtrate was shaken with charcoal, and filtered into 200 c.c. of 5 per cent. aqueous hydrochloric acid. The thiol compound separated as a white solid, and carbonyl sulphide was evolved. The solid was collected and dried in a vacuum over sulphuric acid, when it melted at 133—136° to a clear liquid. The yield was 18·8 grams, or 73 per cent. of the theoretical. It was further purified by dissolving in cold, air-free 5 per cent. aqueous sodium hydroxide, shaking with charcoal, and filtering into excess of 5 per cent. aqueous hydrochloric acid, when pure benzo-*p*-thiol-β-phenylethylamide separated, and melted at 133—136°.

*Benzo-*p*-thiol-β-phenylethylamide* rapidly becomes slightly yellow. In the air it undergoes partial oxidation to the disulphide. This change takes place much more readily in alkaline solution, rendering it difficult to obtain a specimen which dissolves in alkalis without leaving a residue of the disulphide.

It is very readily soluble in the ordinary organic solvents, from which it crystallises in nodules of microscopic needles. The recrystallised solid, however, always contains some disulphide, which remains unmelted at the melting point of the thiol compound. Its solution in alkalis produces a primrose-yellow precipitate on the addition of lead acetate solution. When the pure compound is added to sulphuric acid at 200°, a purple colour is produced, the intensity depending on the quantity of the *p*-thiol compound added. Unlike benzo-*p*-hydroxy-β-phenylethylamide, it does not give a green colour with Mörner's reagent:

0·2493 gave 0·2234 $BaSO_4$. S = 12·3.

$C_{15}H_{15}ONS$ requires S = 12·5 per cent.

*Oxidation of Benzo-*p*-thiol-β-phenylethylamide. Formation of Dibenzodi-β-phenylethylamide* p-*Disulphide* (VIII).

Sixteen grams of benzo-*p*-thiol-β-phenylethylamide, which had not been regenerated through alkaline solution, but had been kept

in a well-corked bottle for three days, were suspended in 200 c.c. of cold 5 per cent. air-free sodium hydroxide solution. A 5 per cent. potassium ferricyanide solution was run in until the supernatant liquid had acquired a permanent yellow tinge, due to excess of the oxidising agent. During the addition of the ferricyanide solution, the disulphide separated in amorphous flocks. The volume of oxidising solution required was 340 c.c., which corresponds with the presence in the initial starting material of 85 per cent. of benzo-*p*-thiol-β-phenylethylamide and 15 per cent. of disulphide. The insoluble disulphide (15·2 grams) was collected, and well washed with water, when it melted at 188—194°. For analysis, it was crystallised from ten times its weight of glacial acetic acid:

0·1453 gave 0·3746 CO_2 and 0·0716 H_2O. C=70·3; H=5·5.
0·2526 „ 0·2292 $BaSO_4$. S=12·5.

$C_{30}H_{28}O_2N_2S_2$ requires C=70·3; H=5·5; S=12·5 per cent.

Dibenzodi-β-phenylethylamide p-*disulphide* crystallises from glacial acetic acid in aggregates of minute needles. In bulk it has the appearance of a white, amorphous powder. It melts at 194—196° (199—201° corr.). It is very sparingly soluble in the ordinary organic solvents at room temperature, but moderately soluble in boiling acetic acid, methyl alcohol, ethyl alcohol, or chloroform, and sparingly so in boiling acetone, benzene, or ethyl acetate. It gives the same colour reaction with sulphuric acid at 200° as is given by the *p*-thiol compound. When finely powdered, it is a very difficult substance to handle, as the particles appear to be very readily electrified by slight rubbing. By prolonged boiling with sodium sulphide solution, the disulphide is reduced to the thiol compound.

The insoluble solid, *A* (p. 227), consisted of impure disulphide, and was purified, with considerable loss, by recrystallisation from acetic acid.

Hydrolysis of Dibenzodi-β-phenylethylamide p-*Disulphide. Formation of Di-β-phenylethylamine* p-*Disulphide Dihydrochloride* (IX).

Six grams of dibenzodi-β-phenylethylamide *p*-disulphide were heated under pressure for four hours at 150° with 60 c.c. of 20 per cent. aqueous hydrochloric acid. When cold, the product was diluted with 300 c.c. of water, and warmed on the water-bath until a clear solution was obtained. This was stirred with charcoal and filtered. The filtrate, on cooling, deposited crystals of the dihydrochloride of di-β-phenylethylamine *p*-disulphide mixed with some benzoic acid, which was removed by four extractions with ether.

The aqueous solution, on filtration, yielded 3·6 grams of the required dihydrochloride, melting and decomposing at 329—331° (339·5—340·5° corr.). On further concentration, the filtrate gave a second crop (0·25 grams) of crystals, melting at 327—329°. The total yield of the required dihydrochloride was thus 87 per cent. of the theoretical.

Di-β-phenylethylamine p-*disulphide dihydrochloride* is most conveniently recrystallised from 5 per cent. aqueous hydrochloric acid. It separates in colourless, microscopic, hexagonal leaflets, which are readily soluble in water, but very sparingly so in 10 per cent. hydrochloric acid solution. It is almost insoluble in boiling 95 per cent. alcohol. With concentrated sulphuric acid at 200° it gives a purple coloration:

0·1565 gave 0·2914 CO_2 and 0·0814 H_2O. C=50·8; H=5·8.
0·2075 „ 0·2588 $BaSO_4$. S=17·2.
0·2002 „ 0·1514 AgCl. Cl=18·7.
$C_{16}H_{20}N_2S_2,2HCl$ requires C=50·9; H=5·9; S=17·0; Cl=18·8 per cent.

The *sulphate* crystallises readily. It is freely soluble in hot water, and separates on cooling in aggregates of silky leaflets.

The *picrate* and *styphnate* were obtained as uncrystallisable oils from aqueous solutions.

The *base* is obtained as an almost colourless oil on addition of aqueous alkalis to an aqueous solution of the hydrochloride. It is soluble in ether or chloroform. On exposure to the air, it readily forms a crystalline carbonate.

Reduction of Di-β-phenylethylamine p-*Disulphide Dihydrochloride. Formation of* p-*Thiol-β-phenylethylamine Hydrochloride* (X).

Di-β-phenylethylamine *p*-disulphide dihydrochloride (3·6 grams) was reduced by means of tin foil (8 grams) and concentrated hydrochloric acid (20 c.c.) in the presence of alcohol (20 c.c.). The solution was allowed to boil vigorously on the water-bath until the dihydrochloride had completely dissolved, which process required about fourteen hours. When quite cold, the complex tin salt which had crystallised out was collected, and dissolved in 200 c.c. of air-free warm water. The tin was completely removed as sulphide, and by rapid concentration of the aqueous solution to a small volume (10 c.c.) the required hydrochloride of *p*-thiol-β-phenylethylamine (2·4 grams) was deposited in a pure state. On further concentration, a second crop (0·2 gram) of slightly less pure salt was obtained. This final mother liquor, and the original mother liquor of the tin salt (the latter freed from tin), were combined and concentrated. The hydrochloride which separated was impure, partial

oxidation to the disulphide having occurred. Accordingly, the solution was oxidised with aqueous ferric chloride, which caused the sparingly soluble dihydrochloride of the starting material to crystallise from the strongly acid solution.

p-*Thiol-β-phenylethylamine hydrochloride* crystallises from dilute aqueous hydrochloric acid or absolute alcohol in colourless, glistening, filmy leaflets of indefinite shape. It is freely soluble in cold methyl alcohol. It melts at 224·5—226° (231·5—233° corr.):

0·1519 gave 0·2808 CO_2 and 0·0853 H_2O. C=50·4; H=6·2.
0·2035 „ 0·2486 $BaSO_4$. S=16·8.
0·2054 „ 0·1553 AgCl. Cl=18·7.

$C_8H_{11}NS,HCl$ requires C=50·6; H=6·4; S=16·9; Cl=18·7 per cent.

p-*Thiol-β-phenylethylamine* is readily obtained by careful neutralisation of an aqueous solution of the hydrochloride with sodium hydroxide solution. It separates in glistening, hexagonal leaflets, which are sparingly soluble in cold water. It is very sparingly soluble in the usual organic solvents, even at their boiling points, but can be readily recrystallised from hot water. It melts at 211—212° (216—217° corr.). With sulphuric acid at 200° it gives a purple colour. Unlike *p*-hydroxy-β-phenylethylamine, it does not respond to Millon's reagent. The base is readily soluble in sodium hydroxide solution, and slowly so in sodium carbonate solution. The alkaline solution gives a primrose-yellow precipitate on addition of lead acetate solution:

0·1210 gave 0·2770 CO_2 and 0·0784 H_2O. C=62·4; H=7·2.

$C_8H_{11}NS$ requires C=62·7; H=7·2 per cent.

The *picrate* is obtained crystalline on the addition of aqueous picric acid solution to a solution of the hydrochloride. It is most conveniently recrystallised from 50 per cent. alcohol, from which it separates in bright orange-yellow needles, melting and decomposing at 154—155° (156·5—157·5° corr.). In alcohol and acetone it is readily soluble, but very sparingly so in benzene:

0·1417 gave 0·2293 CO_2 and 0·0471 H_2O. C=44·1; H=3·7.

$C_8H_{11}NS,C_6H_3O_7N_3$ requires C=44·0; H=3·7 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

[*Received, Dec. 30th*, 1914.]

XXV.—*The Oxidation of Aconitine.*

By George Barger and Ellen Field.

A promising step towards the elucidation of the constitution of aconitine was made by Carr (T., 1912, **101**, 2241), who described a product of oxidation, for which he suggested the formula $C_{23}H_{29}O_9N$ and the name oxonitin. Brady (T., 1913, **103**, 1821) obtained a very similar product, to which he gave the formula $C_{24}H_{29}O_9N$. The price of aconitine makes the yield a matter of importance; Brady obtained only 3 per cent. by oxidation in acid solution and 10—15 per cent. in (at first) neutral solution. Carr's yields were much higher, but variable; his process demands considerable attention to detail. Aconitine permanganate is prepared at 0°, and decomposed by 15 per cent. sulphuric acid at 20—40° in the course of a week or longer. Using Carr's method we generally obtained an amount of oxonitin corresponding with 65—70 per cent. of the theory, although Carr in one or two experiments obtained more than 90 per cent. We have now worked out a simple process by which the yield consistently approaches to the theoretical. The loss in the older experiments was partly due to hydrolysis, by the sulphuric acid employed, and we therefore oxidise by potassium permanganate in acetone solution, a method applied with great success by Leuchs to the oxidation of strychnine (*Ber.*, 1908, **41**, 1711), and also used by one of us in the case of carpaine (T., 1910, **97**, 470). Since aconitine is, however, oxidised only very slowly in acetone solution, we add glacial acetic acid as the oxidation proceeds. The process then is as follows:

Five grams of aconitine are dissolved in 250 c.c. of pure acetone by warming on the water-bath. After cooling, 11 grams of very finely powdered potassium permanganate and 12·5 c.c. of glacial acetic acid are added in the course of five to seven days, each day about one-fifth of both reagents. The acetic acid may be conveniently diluted with acetone to a known volume. The oxidation proceeds at room temperature, and the oxonitin for the most part separates in large crystals on the sides of the flask. When all the permanganate has been reduced, the oxonitin and manganese dioxide are filtered off, washed with acetone, and suspended in water. On passing a current of sulphur dioxide an amount of oxonitin corresponding with 65 per cent. of the theory remains behind in a practically pure condition (melting at 274° without recrystallisation). The rest is obtained in a slightly impure condition by evaporating the acetone and adding water, and after recrystallisation yields an additional 25 per cent.; the total is therefore 90 per cent. of the

theoretical. In order to purify the oxonitin for analysis it can be recrystallised (*a*) by dissolving in fuming hydrochloric acid and diluting with water, (*b*) by dissolving in a mixture of methyl alcohol and chloroform, and adding dry ether, and (*c*) by dissolving in boiling glacial acetic acid and adding acetone; we prefer the third method. The substance then separates in well-formed, stout prisms, melting at 276—277° (bath previously heated to 260°).

Five specimens were analysed. I was prepared by Carr's method and recrystallised by method (*c*) above. The others were prepared by oxidation in acetone solution, III and IV being recrystallised from glacial acetic acid, II by method (*b*) and V by method (*a*). Specimen IV was prepared from japaconitine, and the identity of the oxidation product with that from aconitine itself, which identity had been established by Carr by means of the melting point and specific rotation, is now confirmed by analysis. (We found that IV melted at 277—278°):

I. 0·1270 gave 0·2821 CO_2 and 0·0746 H_2O. C = 60·57; H = 6·53.
II. 0·1488 „ 0·3300 CO_2 „ 0·0874 H_2O. C = 60·48; H = 6·54.
III. 0·1370 „ 0·3038 CO_2 „ 0·0844 H_2O. C = 60·48; H = 6·84.
IV. 0·1200 „ 0·2662 CO_2 „ 0·0728 H_2O. C = 60·50; H = 6·74.
V. 0·1390 „ 0·3108 CO_2 „ 0·0794 H_2O. C = 61·0; H = 6·35.

The mean of these results is C = 60·60, H = 6·60, or, excluding V, where the aberrant results may be due to recrystallisation from fuming hydrochloric acid, C = 60·51, H = 6·66. These figures agree fairly closely with those obtained by Brady (C = 60·7; H = 6·55), but not with those of Carr, who found considerably less carbon. On this account Brady considered his substance to be different from Carr's oxonitin. Our analysis for the oxidation product prepared by Carr's method (specimen I) is, however, in close agreement with the other analyses, and the rather characteristic melting point is identical in whatever way the substance is prepared. We consider, therefore, that the oxidation product is the same in all cases, and Mr. Carr has recently expressed to us his agreement with this view.

The determination of the methoxy-groups gave the following results:

0·2370 gave 0·3265 AgI. MeO = 18·2.
0·1574 „ 0·2256 AgI. MeO = 18·8.
(Brady found 18·2, Carr 19·3.)

The following formulæ may be considered:

$C_{24}H_{29}O_9N$ requires C = 60·60; H = 6·15; 3MeO = 19·2.
$C_{24}H_{31}O_9N$ „ C = 60·35; H = 6·5; 3MeO = 19·1.
$C_{22}H_{29}O_8N$ „ C = 60·7; H = 6·7; 3MeO = 21·4.
$C_{27}H_{35}O_{10}N$ „ C = 60·8; H = 6·6; 3MeO = 17·4.

Of these the first is that of Brady, which does not agree perfectly as regards hydrogen; the second not as regards carbon; the other two not with respect to methoxyl; the third and fourth, moreover, do not agree well with Carr's determination of the acetyl and benzoyl groups, but cannot perhaps be wholly excluded at present.

On heating with fuming nitric acid, oxonitin yields the same oxidation product as aconitine itself, namely, the nitrosocarboxylic acid described by Brady. Of the various methods of degradation which we have tried, we consider the most hopeful to be that of heating with hydriodic acid and phosphorus. This would set free five hydroxyl groups and reduce some of them. 0·3 Gram of oxonitin was heated for five hours with 4 c.c. of hydriodic acid (D 1·96) and 0·3 gram of red phosphorus to 285°. The reaction mixture was diluted with water, treated with sulphur dioxide, and extracted with chloroform. On evaporation of the latter a liquid remained which crystallised on keeping. On recrystallisation from boiling alcohol prisms were obtained, melting at 121—122°, and boiling at about 200°/15 mm. The substance is reprecipitated from alcoholic solution by water, and the suspension is insoluble in acids or alkalis. We have not yet obtained enough for analysis, but the substance must be a relatively simple one.

We wish to express our thanks to the administrators of the Dixon Fund of the University of London for a grant with which the aconitine was purchased.

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[*Received, Feb. 2nd*, 1915.]

XXVI.—*Studies in Catalysis. Part II. The Inversion of Sucrose.*

By ALFRED LAMBLE and WILLIAM CUDMORE MCCULLAGH LEWIS.

IN the first paper of this series (T., 1914, **105**, 2330), it was suggested that the mechanism of homogeneous catalysis was essentially due to radiation of the infra-red type emitted by the catalyst and absorbed by the decomposing substance or substances, thereby raising the internal energy of a certain number of molecules to a critical value, on attaining which such molecules become chemically reactive. The purely physical concept of an "active" molecule

as one which contains the critical energy, and thus differs from an inactive molecule which contains less than this energy, is due to Marcelin. The effect of the catalyst is to increase the number of such active molecules, and thus to increase the velocity of reaction. Rise of temperature was also considered as acting in a similar manner, and the identity of the two effects is made clearer when one considers that an increase in temperature certainly involves an increase in the total infra-red radiation density throughout the system, and therefore an increase in those particular regions which the substance is capable of absorbing. The spectral region over which the hydrogen-ion should emit radiation was calculated (only approximately, of course), and it was shown that over this region $1 \longrightarrow 10\,\mu$ methyl acetate possessed marked absorption. So far as this goes, it supports the radiation view. As a matter of fact, the authors were led to the idea of infra-red radiations as the probable cause of the chemical effects referred to through an erroneous interpretation of the results of the experiments with methyl acetate, from which it appeared that the temperature-coefficient of the constant of hydrolysis was independent of the quantity of catalyst. Further consideration of the problem has shown that, even granting a radiation basis for the phenomena of catalysis, such an idea would likewise involve a diminution in the temperature-coefficient on the addition of positive catalyst provided an appreciable portion of the substance had been activated, that is, provided the reaction was sufficiently sensitive to the catalyst. Similar experiments, reported in the present paper, have been carried out in the case of the inversion of sucrose with varying quantities of hydrochloric acid. In this case, a slight fall in the temperature-coefficient is observed, but the effect is not large. This arises, in part, from the fact that it is only practicable to investigate this reaction over a relatively small range of concentration of the catalyst, during which the relation between the concentration of the catalyst and the velocity-constant does not depart appreciably from the linear function. From the results obtained in the case of reactions not yet published, and in agreement with the conclusions arrived at empirically by Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173), it appears that when the catalytic effect can be examined over a sufficiently wide range, it is found to follow an exponential law, although this also may be an incomplete statement.

At the outset, it is necessary to consider once more the opposed views of chemically active molecules in mass-action equilibrium and the physically active, which are not in any sense in equilibrium. Arrhenius assumes a true mass-action equilibrium between active and inactive molecules, the equilibrium-constant being

$K = \frac{C \text{ active mols.}}{C \text{ inactive mols.}}$, and this equilibrium is also assumed to be attained practically instantaneously. Further, he assumes that the active molecules are so small in number that we can write approximately C inactive mols. $= C$ total substance. He denotes the heat-energy involved in transforming one gram-molecule of inactive to active molecules by q, that is, $\frac{d \log K}{dT} = \frac{q}{RT^2}$. Now the rate at which an observed chemical reaction, such as the inversion of sucrose or the hydrolysis of esters, proceeds is, according to Arrhenius, proportional to $C_{\text{active mols.}}$ That is, $\frac{dx}{dt} = h \times C_{\text{active mols.}} \times W$, where h is the true velocity-constant of the reaction and W the constant concentration of the water. Substituting for $C_{\text{active mols.}}$ its equivalent, namely, $KC_{\text{inactive mols.}} = KC_{\text{total substance}}$, we get

$$\frac{dx}{dt} = hKWC_{\text{substance}} = hKW(a - x).$$

Hence the observed velocity-constant, k, is hKW. Now, Arrhenius writes $\frac{d \log k}{dT} = \frac{q}{RT^2}$, where k is the observed velocity-constant, but q has the significance given above. To realise this, it is necessary to consider that the true velocity-constant, h, does not vary with the temperature. This can be shown thus:

$$\frac{d \log k}{dT} = \frac{d \log hKW}{dT} = \frac{d \log W}{dT} + \frac{d \log h}{dT} + \frac{d \log K}{dT}.$$

But

$$\frac{d \log W}{dT} = 0, \quad \therefore \frac{d \log h}{dT} + \frac{d \log K}{dT} = \frac{q}{RT^2}.$$

But

$$\frac{d \log K}{dT} = \frac{q}{RT^2}, \quad \therefore \frac{d \log h}{dT} = 0.$$

This assumption that the true velocity-constant of the observed reaction is independent of temperature is quite arbitrary, especially so as Arrhenius considers the analogous true velocity-constants active $\rightleftharpoons$ inactive as varying with temperature very considerably.*

Further, Arrhenius considers his theory of active and inactive molecules as capable, not only of accounting for the effect of

* If W be considered as altering with temperature in the sense that

$$\frac{d \log W}{dT} > 0 = \Delta,$$

it would follow that $\frac{d \log h}{dT} + \frac{d \log K}{dT} = \frac{q}{RT^2} - \Delta$, and therefore $\frac{d \log h}{dT} = -\Delta$; that is, h diminishes as temperature increases, which is opposed to the usual notions respecting velocity-constant.

temperature, but also for the effect of added catalyst. That is, he assumes the equilibrium-point, and therefore in this case the value of the equilibrium-constant, K (between active and inactive molecules), to be shifted proportionally to the amount of catalyst. This is quite at variance with the ordinary view of the significance of an equilibrium-constant and its relation to catalysis, for although the work of Lapworth and Jones (T., 1911, **99**, 1427) has shown that large change in the concentration of the catalyst (hydrochloric acid) can shift an ordinary equilibrium-constant, this would not be the case with very small quantities of catalyst. Arrhenius' view assumes that, however small the concentration of the catalyst may be, there is a corresponding change in the value of K. The relation of active molecules to inactive is therefore much more analogous to a stationary state than it is to a mass-action equilibrium. The physical view adopted by Marcelin to explain effects of temperature alone postulates a statistical equilibrium or stationary state, and therefore appears to be much more in accord with facts, since a stationary state can be altered both by temperature and by catalyst. In other words, if we are ever to reach a common basis for both temperature-effect and catalytic effect, it appears necessary to abandon the idea of a mass-action equilibrium active mols. $\rightleftharpoons$ inactive mols., and substitute a stationary state.

Recently, Marcelin's views have been made much more precise by J. Rice in a paper, not yet published, in which it is shown that out of a large number of molecules, a small number may be considered as being in an exceptional state as regards internal potential energy. When this potential energy reaches a certain critical value, V_c, the forces between the parts, which previously were strongly attractive, rapidly become feebly attractive, and the substance may decompose or react. The rate at which the molecules approach this critical surface or critical state would determine the rate of reaction. Rice's final equation is

$$\frac{d \log k}{dT} = \frac{V_c - V_m + \frac{1}{2}RT}{RT^2},$$

where V_m represents the mean potential energy. The numerator may therefore be taken as representing approximately the critical potential increment, which may be denoted by the term E, that is, $\frac{d \log k}{dT} = \frac{E}{RT^2}$, which is formally identical with Marcelin's equation. Rice's equation has been reached by a rigid application of dynamics. Further, Rice has shown that when a positive catalytic effect is present, a negative term is introduced into the numerator, thereby effectively lowering the numerical value of E, such lowering increasing with increase in the concentration of the catalyst.

On the other hand, when a negative catalyst is present, the value of E should be raised. This point will be discussed later. These considerations are sufficient to indicate the preference which may be given to a physical view rather than a chemical one. It must be pointed out, however, that the purely experimental evidence quoted in the previous paper is not sufficient to decide between them, for although the above considerations strongly support the physical concept in contradistinction from the mass-action equilibrium, it is to be expected that, even on the physical view, a very strong positively catalysed reaction should still show a diminution in temperature-coefficient compared with the same reaction when feebly catalysed. Both the Marcelin-Rice view and that of Arrhenius agree in this, that they assume the number of active molecules to be very small compared with the total number present, and it would appear, in the hydrolysis of methyl acetate and sucrose, that the increase in number of active molecules brought about by the addition of even large quantities of catalyst is not sufficient to transform a sensible proportion of the whole into the active state, and hence the temperature-coefficient is only slightly altered.

Apart from the question of the variation of temperature-coefficient with increased concentration of catalyst, the results obtained in the case of the inversion of sucrose are of interest, as they yield data from which the critical increment, E, can be calculated and compared with the energy which the catalysing hydrogen-ions can afford, and at the same time they allow of comparison between the type of radiation emitted by the catalyst and the infra-red regions of absorption exhibited by the sugar.

Experimental.

Polarimeter tubes 4-dcm. in length were used, surrounded by jackets, through which water was circulated by means of a pump from a thermostat. The temperature was thus kept at $25° \mp 0{\cdot}1$. In all cases, 25 c.c. of a 20 per cent. solution of sucrose at 25° were mixed with 25 c.c. of the hydrochloric acid solution, also at 25°, and the mixture then placed in the observation tube. The values of A_0, the angle of rotation at the commencement of the reaction, were calculated as shown by Rosanoff, Clarke and Sibley (*J. Amer. Chem. Soc.*, 1911, **33**, 1911), by plotting the values of $\log A_t - A_\infty$ against t, and extrapolating to $t=0$. The values of A_0 thus obtained are given in brackets in the succeeding tables. The velocity-constants were calculated to the base, e, from the formula $k = \frac{2{\cdot}303}{t} \log_{10} \frac{A_0 - A_\infty}{A_t - A_\infty}$, t being the time in minutes, A_0 the

initial rotation, A_∞ the rotation at $t=\infty$ and A_t the rotation at a time t. Duplicate experiments were in all cases carried out, denoted by (a) and (b). The measurements with 0·900N-hydrochloric acid are given in table I in full, as typical of the degree of accuracy. Table II contains the mean values of each series of measurements, and the mean of the duplicates.

TABLE I.

Inversion by 0·900N-*Hydrochloric Acid at* 25°.

Twenty-five c.c. of a 20 per cent. solution of sucrose added to 25 c.c. of 1·80N-hydrochloric acid:

(a).			(b.)		
t.	A.	$k\times10^3$.	t.	A.	$k\times10^3$.
0·0	[24·09]	—	0·0	[24·05]	—
7·18	21·405	11·18	6·3	21·74	[10·87]
18·00	17·735	11·19	15·45	18·59	11·04
27·05	15·00	11·17	32·37	13·60	11·00
36·80	12·40	11·11	41·08	11·295	11·08
46·00	10·02	11·23	56·08	7·90	11·09
56·07	7·80	11·24	63·25	6·435	11·12
68·02	5·455	11·25	72·10	4·81	11·13
78·02	3·735	11·24	81·10	3·27	11·17
101·70	0·30	11·29	86·12	2·52	11·15
∞	−10·74	—	175·63	−5·955	11·21
		11·21	∞	−10·81	—
					11·11

Mean value of $k=11\cdot16\times10^{-3}$.

TABLE II.

Velocity-constants at 25°.

	$k\times10^3$.		
Hydrochloric Acid.	(1).	(2).	Mean.
0·0502N.	0·4125	0·4214	0·4169
0·2512N.	2·192	2·320	2·255
0·4137N.	4·040	4·047	4·043
0·900N.	11·21	11·11	11·16
1·214N.	17·46	17·45	17·455

Before proceeding to determine the corresponding values of the velocity-constants at 35°, correction had to be made for the change in electrolytic dissociation of the acid with rise in temperature. It was found that the values for the relative viscosity of hydrochloric acid given in the previous paper were too high, and these values have been redetermined. In table III are given the corrected conductivity-data. In this table, N is the normality of the hydrochloric acid, λ the equivalent conductivity, η the relative viscosity, $\lambda\eta$ the corrected conductivity, α the degree of dissociation, and $[H^\cdot]$ the hydrion-concentration ($=\alpha\times N$) in aqueous solution.

TABLE III. (*a*).

Conductivity Data for Hydrochloric Acid at 25°.

N.	λ.	η.	λη.	α.	[H˙].
0·0	424·6	1·0	424·6	—	—
0·5024	359·7	1·034	371·9	0·8760	0·4400
0·8275	341·6	1·064	363·6	0·8563	0·7087
1·280	316·0	1·083	342·2	0·8060	1·031
1·800	290·2	1·119	324·6	0·7645	1·376
2·429	260·2	1·141	296·9	0·6992	1·698

TABLE III. (*b*).

Conductivity Data for Hydrochloric Acid at 35°.

N.	λ.	η.	λη.	α.	[H˙].
0·0	490·3	1·0	490·3	—	—
0·5024	409·1	1·028	420·7	0·8580	0·4309
0·8275	386·2	1·044	403·2	0·8222	0·6805
1·280	355·0	1·088	386·2	0·7875	1·008
1·800	328·3	1·119	367·6	0·7498	1·350
2·429	292·5	1·168	341·6	0·6968	1·692

TABLE III. (*c*).

Conductivity Data for Hydrochloric Acid at 45°.

N.	λ.	η.	λη.	α.	[H˙].
0·0	552·0	1·0	552·0	—	—
0·1005	498·5	1·006	501·3	0·9082	0·09127
0·5024	459·0	1·035	475·0	0·8606	0·4323
0·8275	433·9	1·065	462·0	0·8371	0·6928
1·20	409·0	1·090	445·8	0·8078	0·9694
1·80	372·3	1·129	420·3	0·7614	1·371

The value of λ_∞ was obtained by interpolation from Noyes' data (*Zeitsch. physikal. Chem.*, 1910, **70**, 335).

In determining the velocity-constants for the inversion of sucrose from 25° to 45°, the same total concentrations of acid were employed at each temperature, the results being corrected afterwards for the change in the dissociation of the acid with temperature. The correction involved by this change in dissociation was made by plotting the constants and taking readings corresponding with the concentration of catalyst used at 25°. This correction is given in detail later. The velocity-constants obtained at 35° and 45° are given in tables IV. and V.

TABLE IV.

Velocity-constants at 35°.

Hydrochloric acid.	$k \times 10^3$. (1)	(2)	Mean.
0·0502*N*	1·708	1·769	1·738
0·2512*N*	9·372	9·339	9·355
0·4137*N*	16·95	17·05	17·00
0·900*N*	46·55	46·98	46·76
1·240*N*	76·24	75·71	75·97

TABLE V.

Velocity-constants at 45°.

Hydrochloric acid.	$k \times 10^3$. (1).	(1*a*).	(2).	Mean.
0·0502*N*.	6·157	—	6·269	6·213
0·2512*N*.	34·50	36·77	36·32	35·86
0·4137*N*.	60·01	—	61·24	60·62
0·900*N*.	149·1	142·6	154·9	148·8

In the case of 0·900*N*-hydrochloric acid at 45°, the measurement of the constants was very difficult, the whole reaction proceeding to completion in half-an-hour. To obtain the temperature-coefficients the velocity-constants at 35° and 45° must be corrected for the change in dissociation of the hydrochloric acid with rise in temperature. In the experiments on the hydrolysis of methyl acetate the velocity-constants at the two temperatures were referred to the same hydrion concentration. This has been done in the present case, the values obtained being given in the following tables.

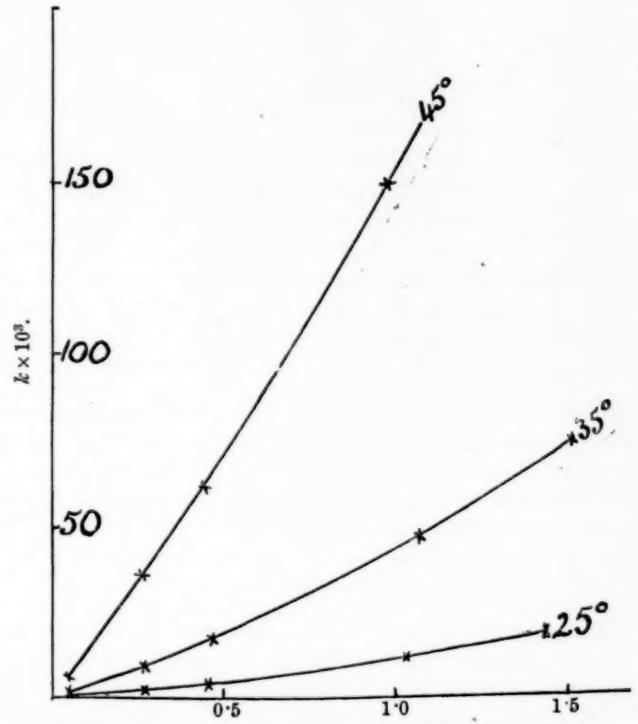
TABLE VI. (*a*).

Normality of hydrochloric acid at 25°.	Normality at 35°.	Hydrion concentration.	k_{35}/k_{25}.
0·0502	0·0502	0·048	4·16
0·2512	0·2512	0·242	4·15
0·4137	0·4137	0·374	4·20
0·900	0·928	0·764	4·39
1·214	1·240	0·985	4·35

TABLE VII. (*a*).

Normality of hydrochloric acid at 35°.	Normality at 45°.	Hydrion concentration.	k_{45}/k_{35}.
0·0502	0·0502	0·048	3·58
0·2512	0·2512	0·242	3·82
0·4137	0·4137	0·374	3·56
0·928	0·910	0·764	3·08

In view, however, of the work which has been done on the probable catalytic effect of the undissociated molecule of hydrochloric acid, it seems more justifiable that comparison should be made under conditions which allow for the catalytic effect of the undissociated molecule. To obtain truly comparable temperature-coefficients we proceed as follows: The catalytic effect of the undissociated molecule of hydrochloric acid at 25° is about twice that of the hydrogen ion. Hence if N be the normality of a solution of



Total catalytic effect in terms of hydrogen-ion concentration.

hydrochloric acid at 25°, α its degree of dissociation, the total catalytic effect in terms of the hydrogen ion is given by:

$$\alpha N + 2(1 - \alpha N) = N(2 - \alpha).$$

At 45° McBain (T., 1914, **105**, 1517) has calculated the catalytic effect of the undissociated molecule to be 1·5 times that of the hydrogen ion. The value has been used therefore at 45°. The values of k were plotted against the total catalytic effect expressed in terms of the hydrogen ion of the acid solutions used at 25°, 35°, and 45°, and are reproduced in the diagram. From the resulting curves the

values of k were obtained at 35° and 45°, for the same total catalytic effect as had been used at 25°. The values of the temperature-coefficients thus obtained are given in the following tables:

TABLE VI. (*b*).

Temperature-coefficients between 25° *and* 35°.

Total catalytic effect in terms of hydrogen ions.	Mean k_{25}.	Mean k_{35}.	k_{35}/k_{25}.
0·0531	$0{\cdot}4169\times10^{-3}$	$1{\cdot}738\times10^{-3}$	4·16
0·2756	$2{\cdot}256\times10^{-3}$	$9{\cdot}355\times10^{-3}$	4·15
0·4624	$4{\cdot}043\times10^{-3}$	$16{\cdot}70\times10^{-3}$	4·13
1·045	$11{\cdot}16\times10^{-3}$	$45{\cdot}75\times10^{-3}$	4·10
1·444	$17{\cdot}45\times10^{-3}$	$71{\cdot}70\times10^{-3}$	4·10

TABLE VII. (*b*).

Temperature-coefficients between 35° *and* 45°.

Total catalytic effect in terms of hydrogen ions.	Mean k_{35}.	Mean k_{45}.	k_{45}/k_{35}.
0·0531	$1{\cdot}738\times10^{-3}$	$6{\cdot}213\times10^{-3}$	3·58
0·2756	$9{\cdot}355\times10^{-3}$	$37{\cdot}30\times10^{-3}$	3·98
0·4624	$16{\cdot}70\times10^{-3}$	$64{\cdot}50\times10^{-3}$	3·86
1·045	$45{\cdot}75\times10^{-3}$	$160{\cdot}50\times10^{-3}$	3·51

The values of the constants have not been stoicheiometrically corrected for the water present. That is, they are really kW values, but as W remains practically constant throughout the series of experiments, this correction would not influence the comparison of the constants at different temperatures.

Discussion of Results.

From the diagram it will be seen that the curves ascend more steeply than a linear function would require. Presumably, if a sufficiently wide range could be examined the curves would be exponential in character. The physical (or chemical) significance of the divergence from the straight line is evidently that the catalytic efficiency of a given catalysing molecule or ion is increased by the presence of other molecules or ions of the catalyst present, so that on, say, doubling the concentration of the catalyst, we not only double the catalytic effect, but cause a slight further increase owing to the increased efficiency of each individual. This is quite in agreement with what one would expect from the point of view of radiation. According to the theory of radiation the time τ between two consecutive emissions of a quantum ($h\nu$) from a resonator is given by the expression $\tau = \frac{3Lh\nu}{\pi u_\nu}$, where L is a

constant for a catalysing molecule or ion (depending on its mass and charge) and u_ν is the radiation density in the medium for the frequency ν. As we increase the number of catalyst particles (having a characteristic vibration-frequency ν) it is known on the basis of the classical electromagnetic theory as well as on Planck's modification of the theory that u_ν increases. Hence an addition of catalyst, by increasing u_ν diminishes τ, and therefore increases the rate with which a given catalytic particle emits, that is, increases the efficiency of the particle, so that the total catalytic effect increases more rapidly than the concentration.

As already pointed out, the hydrogen ion probably yields radiation of wave-length lying between 1 and 10μ. An examination of the infra-red absorption spectrum of sucrose shows that this substance, like methyl acetate, has marked absorption in this region, and hence the radiation emitted by the catalyst is of the absorbable type. It may be pointed out here, that water has marked absorption in this, as in other regions, and therefore the influence of the hydrogen ions may be to make active the water molecules, or, indeed, to activate a sugar–water complex, the existence of such complexes having been postulated by several workers in this field.

We are now in a position to calculate the critical increment E for sucrose, that is, the extra amount of energy which 1 gram-molecule of the system requires according to the Marcelin-Rice equation, $\frac{d \log k}{dT} = \frac{E}{RT^2}$. This may be transformed into $\log_e \frac{k_{35}}{k_{25}} = \frac{E}{R}\left(\frac{1}{298} - \frac{1}{308}\right)$ for the temperature-range 25° to 35°. Since for the mean value of $\frac{k_{35}}{k_{25}}$ we can take 4·13, we obtain for E the value 26,000 calories per gram-molecule. Hence each single molecule, in order to become "active," requires $\frac{26{,}000}{6{\cdot}85 \times 10^{23}}$ calories or $1{\cdot}6 \times 10^{-12}$ ergs. Applying Einstein's law that one molecule reacts by absorbing one quantum ($=h\nu$), where h is Planck's constant, and ν is the vibration-frequency of the radiant energy absorbed, we can equate $h\nu$ to E per molecule. Hence

$$\nu = \frac{1{\cdot}6 \times 10^{-12}}{6{\cdot}55 \times 10^{-27}} = 2{\cdot}44 \times 10^{14}.$$

The wave-length corresponding with this is $1{\cdot}23 \times 10^{-4}$ cm. ($=1{\cdot}23\mu$). This lies, as already pointed out, in the region of absorption of sucrose, and hence it follows, as in the case of methyl acetate, that the mechanism whereby the velocity of the reaction is increased by increase in temperature, can be accounted for on a radiation view as far as position of absorption is concerned.

In a similar way we may calculate the value of E for the temperature-range 35° to 45°, and taking 3·73 as the mean value of the temperature-coefficient, we obtain E equal to 25,800 calories per gram-molecule, or $1{\cdot}58 \times 10^{-12}$ ergs, a quantity practically identical with that required per molecule for the range 25° to 35°.

The Absolute Value of the Speed of a Reaction.

The velocity-constant is directly proportional to the number of molecules approaching the "critical surface" per second; the greater this number the greater the velocity of reaction. Now the nearer the "critical surface" is to the mean position of potential energy, the greater will be the number of molecules approaching the critical surface per second, and hence the greater the speed of the reaction at a given temperature. The closer the critical state is to the mean state, however, the smaller obviously is the critical increment E; that is a small value of E, and consequently a small temperature-coefficient, should correspond with a large value of velocity of reaction, provided the conditions respecting the solvent are sufficiently comparable. It would follow from this that if the speed of a particular reaction in a given solvent be lowered by addition of some second substance or solvent, we should expect that the value of E would be correspondingly increased. This appears to be borne out by the following measurements carried out by H. von Halban (*Zeitsch. physikal. Chem.*, 1909, **67**, 129). The unimolecular velocity constant for the decomposition of triethylsulphine bromide at 60° in pure acetone was found to be 0·0077. In acetone +4·03 per cent. of water, the velocity-constant was 0·00063. In acetone+10 per cent. of water the constant was 0·000044. That is to say, the addition of water depresses the speed of this reaction in acetone (the effect being an exponential function of the concentration of the water). From the data given by von Halban, it is possible to calculate the numerical values of E; they are respectively 29,720, 31,320, and 32,240 calories per gram-molecule. Hence the decrease in velocity-constant corresponds with an increase in E. The same phenomenon is observed in the case of the decomposition of oxalic acid in absolute sulphuric acid (Bredig and Lichty, *Zeitsch. Elektrochem.*, 1906, **12**, 459; *J. Physical Chem*, 1907, **11**, 225). The speed of the reaction is extremely sensitive to the addition of small amounts of water. The values of k and E are shown in the following table:

Percentage of water.	k.	E in calories per gram-mol.
0·1	$k_{35°}/k_{25°} = 4{\cdot}42$.	27,300
0·6	$k_{45°} = 0{\cdot}0005746$; $k_{70°} = 0{\cdot}01814$;	28,760
3·0	$k_{70} = 0{\cdot}00094$; $k_{98°} = 0{\cdot}02365$;	29,200

Here again a decrease in k is accompanied by an increase in E. (It may be pointed out that Lichty has assumed E independent of temperature, and therefore the increase in E should be slightly more marked than that given.)

Yet another example is furnished by the work of Lobry de Bruyn and Sluiter (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **6**, 773), on the transformation of acetophenoneoxime to acetanilide in solution in sulphuric acid. The speed increases the more nearly pure the acid, that is, the less the percentage of water, the water functioning as before as a negative catalyst. On setting out the results it will be found that the effect of the water is an exponential function of the concentration as in the decomposition of triethylsulphine bromide. The following results were obtained in this case, the reaction being unimolecular, and k denoting the velocity-constant:

At 60° with 93·6 per cent. sulphuric acid, $k=0{\cdot}0011$.
At 65° „ 93·6 „ „ „ „ $k=0{\cdot}0019$.
At 60° „ 94·6 „ „ „ „ $k=0{\cdot}0013$.
At 65° „ 94·6 „ „ „ „ $k=0{\cdot}0021$.

Hence with 94·6 per cent. sulphuric acid the temperature-coefficient (for 5°) is $\frac{0{\cdot}0021}{0{\cdot}0013}=1{\cdot}62$, whence $E=21{,}720$ calories.

With 93·6 per cent. sulphuric acid the temperature-coefficient is $\frac{0{\cdot}0019}{0{\cdot}0011}=1{\cdot}73$, and $E=24{,}670$ calories. That is, with increase of concentration of water the absolute velocity falls, and simultaneously the critical increment E rises.

In these reactions water acts as a strong anticatalyst with regard to acetone and sulphuric acid respectively. On the radiation view this is to be explained by the hypothesis that the water molecules absorb some of the radiation emitted by the acetone and sulphuric acid molecules, which would otherwise have been effective in catalysing the reaction. That is to say, the critically reactive state is effectively removed to a greater distance from the mean value, when water is present, than is the case in acetone or sulphuric acid alone; and hence a fewer number of molecules reach the active state per second, thus decreasing the velocity. In other words, the critical increment is effectively increased. Several other reactions in which water is considered to act anticatalytically are known, for example, the hydrolysis and formation of esters, but no data for calculation appear to be available.

Comparable conditions for the comparison of k and E values are most fully realised in the case of a reversible reaction in a given solvent. In a few cases the necessary data for comparing k and E

are available. Thus Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 625) has investigated the change of carbamide to ammonium cyanate in aqueous solution with acid catalyst present at 90·1° and 99·2°. For the mean temperature 94·6°, the value of k, carbamide $\longrightarrow$ cyanate, is $1{\cdot}71 \times 10^{-3}$, and the value of E is 33,900 cals., a fairly high value. On the other hand, for the reverse reaction at the same mean temperature, 94·6°, the velocity-constant is 4·0, the value of E being 20,020, that is, less than before. Hence the larger absolute velocity is accompanied by the smaller E for the reasons given.

A more striking case still is that investigated by von Halban (*loc. cit.*), in which the rate of decomposition and the rate of formation of *p*-bromophenyldimethylallylammonium bromide has been measured in tetrachloroethane and chloroform respectively between the limits 25° and 35°. In the case of the decomposition in tetrachloroethane the velocity-constant at 25° is 0·000078; the value of E we have calculated to be 28,790 calories, that is, a large quantity, whilst the rate of formation at the same temperature is 0·0017, the value of E being 9738 calories, a much smaller quantity. That is, the larger velocity-constant has the smaller value of E. Similarly, in chloroform solution the velocity-constant for the decomposition at 25° is 0·000027, and the value of E 30,620, whilst the rate of re-combination at the same temperature is 0·00055, and the value of E 11,790.

Another example is that of the action of hydrochloric acid on ethyl alcohol in mixtures containing considerable quantities of alcohol and water. This has been re-investigated by Kilpi (*Zeitsch. physikal. Chem.*, 1914, **86**, 427), and he has found that the reaction is mainly due to the action of the undissociated part of the acid. The reaction reaches an equilibrium, and Kilpi gives the data for the velocity-constants of the direct and reverse reactions at 97° and 110°. Denoting by k_1 the velocity-constant of the action of the acid on the alcohol, and by k_2 the constant for the action of water on ethyl chloride, Kilpi found:

$$k_{1\ 110°} = 0{\cdot}86 \times 10^{-3}$$
$$k_{1\ 97°} = 0{\cdot}167 \times 10^{-3},$$

whence $\frac{k_{1\ 110°}}{k_{1\ 97°}} = 5{\cdot}1$ and $E = 35{,}490$ calories per gram-molecule.

Also

$$k_{2\ 110°} = 1{\cdot}85 \times 10^{-3}$$
$$k_{2\ 97°} = 0{\cdot}59 \times 10^{-3},$$

whence $\frac{k_{2\ 110°}}{k_{2\ 97°}} = 3{\cdot}1$. $E = 24{,}650$ calories.

That is, the greater the absolute velocity, the smaller is the temperature-coefficient, and consequently the smaller the E value

when the conditions regarding solvent are comparable. These instances, which refer to reactions under comparable conditions, serve to substantiate what has been said regarding the relation of k to E.

When, however, we attempt to compare the effect of various solvents on one and the same reaction, a small value of k does not necessarily mean a large value of E, for these are not sufficiently comparable conditions. Approximate agreement is actually reached in the case of the decomposition of triethylsulphine bromide in various solvents, at one and the same temperature, as is evidenced in the results obtained by von Halban (*loc. cit.*), in which six out of the eight solvents examined, namely, benzyl alcohol, acetic acid, ethyl alcohol, propyl alcohol, amyl alcohol, chloroform, nitrobenzene, tetrachloroethane, and acetone, form a series of ascending k values with a series of descending E values. The exceptions are acetic acid and nitrobenzene. On the other hand, the data obtained by Dimroth (*Annalen*, 1910, **377**, 128) for the change of methyl 5-hydroxy-1-benzyl-1:2:3-triazole-4-carboxylate into the anilide of methyl diazomalonate in the solvents methyl alcohol, ethyl alcohol, acetone, and chloroform exhibit values of k which do not vary inversely as E. In general a larger k is accompanied by a larger temperature-coefficient. Hence in applying the principle, namely, that the larger the value of k the smaller is the value of E, it is essential to maintain comparable conditions as regards the solvent. This, as pointed out, is most fully realised in the case of a reversible reaction in a given solvent, and sufficiently nearly realised in the case of moderate additions of a second solvent, such as water, to the system in question.

The Catalytic Activity of the Undissociated Molecule.

In the previous paper the catalytic activity of the hydrogen-ion was considered from the radiation point of view, the mechanism of the production of quanta being ascribed to the vibrations of the charged particle over a distance of the order 10^{-8} of a cm., that is, of the order of a diameter of a molecule. Similar vibrations equally capable of emitting infra-red quanta may be anticipated from an undissociated molecule such as hydrochloric acid, if we assume, as is generally done, that the hydrogen atom, electrically charged, exists as a definite entity in the molecule, and vibrates with respect to the chlorine. Thus the attributing of a catalytic effect to the molecule is not at variance with the radiation view. Further, the real distinction between a strong electrolyte and a weak electrolyte lies in the fact that the undissociated molecule of a strong electrolyte (hydrochloric acid) has its constituent parts less firmly held

together, that is, more easily dissociable than is the case with the weak electrolyte (acetic acid). In the undissociated molecule of a strong electrolyte we therefore expect greater freedom of movement of the relative parts of the molecule, and hence a greater opportunity for the emission of quanta, and therefore a greater catalytic activity than is the case with the weak electrolyte. This is in agreement with the facts so far as they are known.

Summary.

(1) Measurements have been made of the rate of inversion of sucrose by hydrochloric acid at 25°, 35°, and 45°, the concentration of the acid being varied over a considerable range, from which the values of the temperature-coefficients and their change with the concentration of the catalyst have been determined.

(2) It is shown that there is a slight fall in the critical increment E as the concentration of the catalyst increases, when comparison of the constants is made on the assumption that the undissociated molecule is active as well as the ions.

(3) An examination of the literature demonstrates that for reversible reactions the larger the velocity-constant the smaller is the value of E, and vice versa. This also holds true when the nature of the solvent is altered to a certain extent by the addition of a second solvent.

(4) The conclusions reached in (2) and (3) are in agreement with Rice's modification of the Marcelin equation, and also in agreement with the theory that chemical reactivity is due to infra-red radiation.

(5) The possible catalytic action of the undissociated molecule has been discussed from the radiation point of view.

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[*Received, Dec. 23rd,* 1914.]

XXVII.—*The Constitution of the Aminoazo-compounds.*

By Edward Charles Cyril Baly and Robert Ernest Victor Hampson.

From the point of view of their constitution the changes of colour exhibited by aminoazobenzene in various solvents are of some importance. It has appeared to be such a simple matter to explain the bluish-red colour of aminoazobenzene hydrochloride by attri-

buting to it the quinonoid structure, $C_6H_5\cdot NH\cdot N{:}C_6H_4{:}NH_2Cl$, and this formula certainly appears at first sight to be supported by the fact that the ammonium salt, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NMe_3I$, is yellow in solution, and that its absorption spectrum is quite different from that of aminoazobenzene hydrochloride (Hewitt and Thole, T., 1910, **97**, 511).

Further investigations, however, reveal considerable difficulties in the way of this simple explanation. These difficulties were first recognised by Hantzsch (*Ber.*, 1909, **32**, 2129), who noted the fact that azo-compounds, when dissolved in concentrated sulphuric acid, develop marked colours, and further that the absorption of such solutions is very characteristic. The absorption spectrum of a solution of aminoazobenzene in concentrated sulphuric acid is entirely different from that of aminoazobenzene hydrochloride. Hantzsch therefore proposed three possible formulæ for the constitution of the salts of aminoazobenzene:

$$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH_2HX.$$
(I.) Ammonium salt.

$$C_6H_5\cdot N_2(HX)\cdot C_6H_4\cdot NH_2.$$
(II.) Azoid formula.

$$C_6H_5\cdot NH\cdot N{:}C_6H_4{:}NH_2X.$$
(III.) Quinonoid formula.

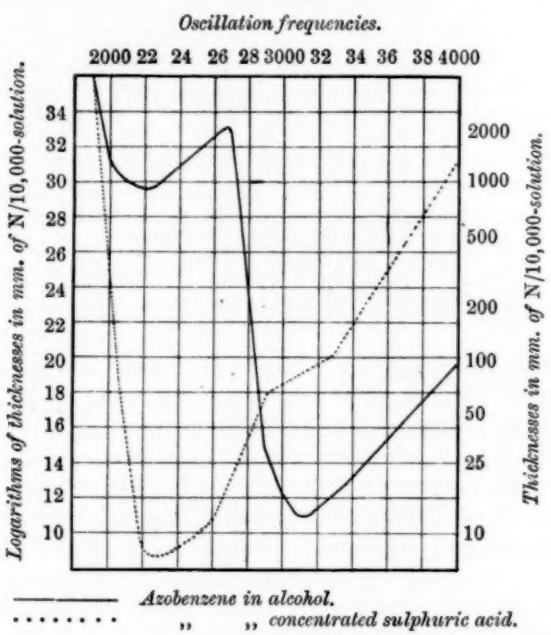
Each of these formulæ, according to Hantzsch, is characterised by a definite type of absorption spectrum. The first of these is exhibited by benzeneazophenyltrimethylammonium iodide, and as no doubt exists as to the constitution of this compound its absorption spectrum typifies that of all compounds having formula I. There are left two types of absorption spectra, one of which is shown by solutions of the azo-compounds in concentrated sulphuric acid, and the other by aminoazobenzene hydrochloride. Hantzsch therefore states that these compounds in concentrated sulphuric acid have formula II, and that the hydrochlorides have formula III. He bases his conclusions mainly on the fact that azobenzene, aminoazobenzene, and benzeneazophenyltrimethylammonium iodide give almost identical absorption curves when dissolved in concentrated sulphuric acid. Hantzsch and Hewitt therefore agree as regards the constitution of aminoazobenzene hydrochloride.

We have re-investigated the absorption spectra of these compounds, and have found that these explanations do not satisfy all the facts, and we have made one observation which appears entirely to have escaped the notice of Hewitt and Thole, and of Hantzsch. In preparing solutions of aminoazobenzene hydrochloride it is sufficient to add 1 per cent. of hydrochloric acid to an alcoholic solution

of the parent base when the characteristic bluish-red colour is developed.

If now 1 per cent. of hydrochloric acid is added to an alcoholic solution of benzeneazophenyltrimethylammonium iodide the solution turns red and exhibits an absorption spectrum which is quite different from that of the parent compound in neutral alcoholic solution or in solution in concentrated sulphuric acid. The importance of this observation is manifest, for it is obvious that whatever be the explanation of the change of colour of aminoazobenzene when hydrochloric acid is added to its solution, the same explana-

FIG. 1.


Oscillation frequencies.
2000 22 24 26 28 3000 32 34 36 38 4000
Logarithms of thicknesses in mm. of N/10,000-solution.
34 32 30 28 26 24 22 20 18 16 14 12 10
2000 1000 500 200 100 50 25 10
Thicknesses in mm. of N/10,000-solution.
Azobenzene in alcohol.
,, ,, concentrated sulphuric acid.

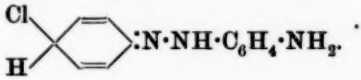
tion must hold good for the ammonium salt. It seems impossible, therefore, for the change of colour of aminoazobenzene to be due to the formation of the quinonoid salt, $C_6H_5{\cdot}NH{\cdot}N{:}C_6H_4{:}NH_2Cl$, since this cannot be adopted for the ammonium salt.

Again, there is a further difficulty in accepting Hantzsch's conclusions for the following reason. The addition of a small quantity of sulphuric acid to an alcoholic solution of aminoazobenzene gives a colour exactly the same, with the same absorption spectrum as with 1 per cent. of hydrochloric acid. According to Hantzsch this must be due to the formation of the compound

$$C_6H_5{\cdot}NH{\cdot}N{:}C_6H_4{:}NH_2{\cdot}HSO_4,$$

yet on dissolving the base in concentrated sulphuric acid the salt now has the formula, $C_6H_5 \cdot N_2(H_2SO_4) \cdot C_6H_4 \cdot NH_2$. It is a fair question to ask why the acid molecule changes its position, and at what concentration of acid this interesting event takes place.

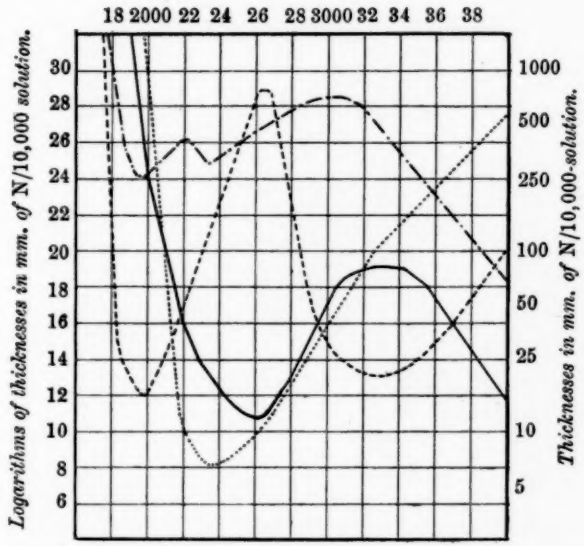
. There is, we are aware, still left an alternative formula which might be put forward, namely,



In case such a suggestion as this be made we would point out that

FIG. 2.

Oscillation frequencies.

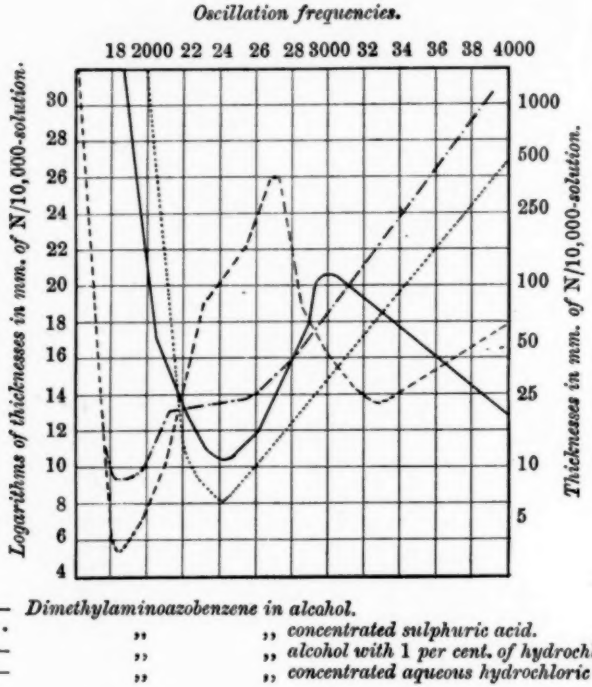


———— *Aminoazobenzene in alcohol.*
. . . . . ,, ,, *concentrated sulphuric acid.*
— — — — ,, ,, *alcohol with 1 per cent. of hydrochloric acid.*
— • — • — ,, ,, *concentrated aqueous hydrochloric acid.*

if it were possible that such a configuration be formed it should occur with azobenzene itself. Azobenzene is not, however, influenced by small quantities of hydrochloric acid, and in the presence of a large excess of acid it shows an absorption identical with the other azo-compounds in concentrated sulphuric acid solution. It seems very certain, therefore, that some other explanation must be found for the colour of aminoazobenzene hydrochloride than the one adopted by Hewitt and by Hantzsch.

The absorption curves of azobenzene, aminoazobenzene, dimethylaminoazobenzene, and benzeneazophenyltrimethylammonium iodide in various solvents are given in Figs. 1—4, and they show remarkable analogies. Azobenzene in alcoholic solution shows two absorption bands at about $1/\lambda$ 2240 and 3160; in solution in concentrated sulphuric or hydrochloric acid it shows only the first band at $1/\lambda$ 2280. Now it has been proved in previous papers that it is not possible to explain any definite absorption curve by attributing it to a definite primary structure. It is far simpler to deal with

FIG. 3.

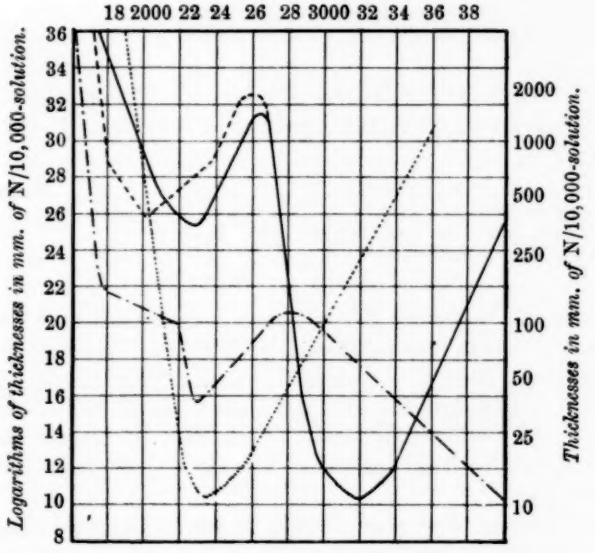

Oscillation frequencies.
18 2000 22 24 26 28 3000 32 34 36 38 4000
Logarithms of thicknesses in mm. of N/10,000-solution.
30 28 26 24 22 20 18 16 14 12 10 8 6 4
1000 500 250 100 50 25 10 5
Thicknesses in mm. of N/10,000-solution.
Dimethylaminoazobenzene in alcohol.
,, ,, concentrated sulphuric acid.
,, ,, alcohol with 1 per cent. of hydrochloric acid.
,, ,, concentrated aqueous hydrochloric acid.

absorption bands as evidences of the power possessed by the molecules of absorbing definite light waves, this power depending on the state to which the closed field of force surrounding the molecules is opened by means of the solvent. Azobenzene therefore in alcoholic solution exists in two such stages each with its power of absorbing definite light-waves. In concentrated sulphuric acid, on the other hand, the compound has its field of force opened up only to one of these two stages, so that only one absorption band is shown.

Aminoazobenzene shows only one band in alcoholic solution, and therefore its closed field of force is opened only to one stage characterised by its power of absorbing light of a wave-length of about $1/\lambda = 2610$. In concentrated sulphuric acid solution it is opened up to another stage with power of absorbing light of wave-length $1/\lambda = 2370$, and is therefore analogous to azobenzene in the same solvent. In alcoholic solution containing 1 per cent. of hydrochloric

FIG. 4.

Oscillation frequencies.



———— *Benzeneazophenyltrimethylammonium iodide in alcohol.*

. . . . . " " " *concentrated sulphuric acid.*

— — — — *Benzeneazophenyltrimethylammonium iodide in alcohol with 1 per cent. of hydrochloric acid.*

—·—·— *Benzeneazophenyltrimethylammonium iodide in concentrated aqueous hydrochloric acid.*

acid two bands are shown at $1/\lambda = 1980$ and 3300, so that here again two stages co-exist, and of these one is the same as that of azobenzene in alcohol. In a solution in concentrated hydrochloric acid two bands again are shown, but one of these is the same as in dilute hydrochloric acid solution ($1/\lambda = 1970$), whilst the other is the same as in concentrated sulphuric acid solution. Altogether, therefore, aminoazobenzene shows four absorption bands according to the solvent, and the frequencies of these may be arranged as follows:

Alcohol			2610	
Concentrated sulphuric acid		2370		
One per cent. alcoholic hydrochloric acid	1980			3300
Concentrated hydrochloric acid	1970	2360		

Dimethylaminoazobenzene in alcoholic, 1 per cent. alcoholic hydrochloric acid and concentrated sulphuric acid solutions is very similar to aminoazobenzene. In concentrated hydrochloric acid solution it differs in that the first band at $1/\lambda = 1850$ has deepened at the expense of the second band, which has shrunk to a step-out. The bands can be arranged as follows:

Alcohol		2420	
Concentrated sulphuric acid		2420	
One per cent. alcoholic hydrochloric acid	1850		3260
Concentrated hydrochloric acid	1850	2420 (step-out)	

Exactly analogous results are obtained with benzeneazophenyltrimethylammonium iodide, the bands of which can be arranged as follows:

Alcohol		2290	3190	
Concentrated sulphuric acid		2340		
One per cent. alcoholic hydrochloric acid	2010			3190
Concentrated hydrochloric acid	2010 (step-out)	2300		

This substance therefore lies between azobenzene and its amino-derivatives. Its alcoholic solution is very similar in absorptive power to azobenzene, but it develops the long wave-length band at $1/\lambda = 2010$ in the presence of small quantities of hydrochloric acid just as do the amino-compounds. This fact, as already stated, is clearly opposed to the quinonoid formula for aminoazobenzene hydrochloride.

During the past few years Hantzsch has definitely taken up the position that an absorption curve is characteristic of a particular primary structure. It is necessary for him, therefore, if he maintains this position, to invent a new formula for aminoazobenzene when in solution in concentrated hydrochloric acid, for its absorption curve differs from those to which he assigned the formulæ I, II, and III above. Then, again, yet a different formula still would have to be invented for dimethylaminoazobenzene hydrochloride, for it again is different. Similarly, he must also find new formulæ for benzeneazophenyltrimethylammonium iodide in 1 per cent. alcoholic hydrochloric acid and in concentrated hydrochloric acid.

As a matter of fact, however, there is no need for any such formulæ. As already pointed out, the whole of the phenomena can be explained in the simplest possible manner by the conception of the molecular fields of force and the opening-up of these by the solvent with the result that other light waves are absorbed. Con-

sidering all the four substances here dealt with, they all can show four absorption bands, that is to say, the power of absorbing light of four different frequencies, namely, about $1/\lambda = 1900$, 2300, 2600, and 3200. The nature of the solvent determines which of these different powers of absorption are called into play. The effect of the solvent depends to a certain extent on the nature of the affinity of the molecule, that is to say, whether we take azobenzene, amino-azobenzene, or benzeneazophenyltrimethylammonium iodide. Each power of absorbing a definite light-vibration is characteristic of the molecules of the azo-compounds dealt with, but these powers are latent, and are called into play by the use of the proper solvent. The fact that the molecules become endowed with a new power of absorption of light in a new solvent simply means that a previously latent vibration period is rendered active by that solvent. The existence of several possibilities possessed by one and the same substance of absorbing different light-waves has been discussed by one of us in another paper (Baly, *Phil. Mag.*, 1914, [vi], **27**, 632). It was shown that all such absorption bands in the ultra-violet and visible regions of the spectrum are directly connected with a fundamental vibration in the infra-red. This fundamental vibration is known to be characteristic of the substance itself, and not of any structural isomeride, and therefore the visible and ultra-violet absorption bands must also be characteristic of the substance itself and not of any structural isomeride. To attempt to explain all such absorptive powers by different structural formulæ only leads to an impasse, as, indeed, Hantzsch himself recently recognised when he stated that there are not enough structural formulæ possible to satisfy all the absorption spectra observed.

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[*Received, Jan. 4th*, 1915.]

XXVIII.—*Note on the Nitroguaiacols.*

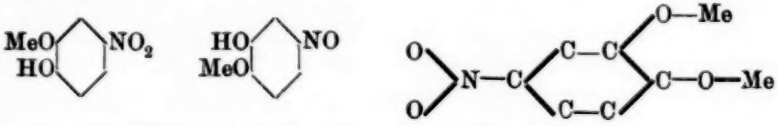
By DAVID CARDWELL and ROBERT ROBINSON.

THE two nitroguaiacols, the isomeric monomethyl ethers of 4-nitrocatechol, have been previously prepared, but have been identified as one single substance. Thus Rupe (*Ber.*, 1897, **30**, 2446) obtained 4-nitroguaiacol (I) by the oxidation of nitrosoguaiacol by means of potassium ferricyanide in alkaline solution, a method which establishes the constitution of the product, and Cousin (*J. Pharm. Chim.*, 1899, [vi], **9**, 276) subsequently described the product of nitration of

acetylguaiacol as the acetyl derivative of the same nitroguaiacol. This substance is, however, the acetyl derivative of 5-nitroguaiacol (II), the nitration being directed to the para-position by the methoxy- rather than by the acetoxy-group.

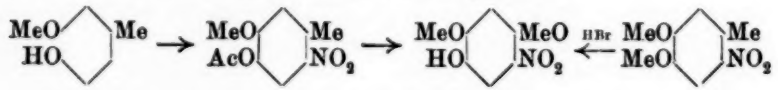
The two isomerides are obtained from nitroveratrole by a process of hydrolysis, and alkaline agents convert the methoxy-group in the para-position with respect to the nitro-group into hydroxyl, and so produce 4-nitroguaiacol, whereas acid hydrolysis affects the meta-methoxy-group and produces 5-nitroguaiacol. This interesting and rather unexpected result may receive some explanation if the distribution of affinity in nitroveratrole is considered in the light of the theories of Werner and Flürscheim.

This distribution is shown in III, in which the thickened lines represent strengthened affinities, and it will be seen that the point of attack for hydroxyl ions would be at the para-position with respect to the nitro-group, whilst the methyl group of the meta-methoxy-group would be the more likely to be removed by means of hydrogen ions:



(I.) (II.) (III.)

6-Nitrohomoveratrole is not readily attacked by alkali hydroxides, but we have included evidence which shows that in this case also hydrobromic acid hydrolyses the methoxy-group in the meta-position with respect to the nitro-group. The relations which justify this statement are illustrated in the following scheme:



Should it be desired to determine whether a particular specimen is 4- or 5-nitroguaiacol, the best method would be a comparison, by means of the method of mixed melting points, with 5-nitroguaiacol, very readily obtained in the form of its acetyl derivative by the nitration of acetylguaiacol.

Experimental.

Conditions of Nitration of Veratrole.

Veratrole is very easily nitrated, but is not affected by a moderately concentrated solution of nitric acid in ether. Aqueous nitric acid containing only 1 part of nitric acid (D 1·42) in 10 parts of

water nitrates the substance at room temperature quantitatively in two to three days, whilst more concentrated solutions naturally effect the substitution more readily. A 99 per cent. yield of 4-nitroveratrole is obtained when veratrole (25 grams) is gradually added, with careful cooling, to a mixture of nitric acid (20 c.c., D 1·42) and water (20 c.c.). This product was fractionally crystallised, and found to be entirely free from any isomeric nitro-compound.

5-Nitroguaiacol (II).

Several experiments were made in order to determine the conditions under which the hydrolysis of nitroveratrole by acids is best accomplished, and concentrated hydrobromic acid at 98° was finally chosen as the reagent, mainly on account of the absence of decomposition products of a tarry nature when the reaction was so carried out.

(*a*) Nitroveratrole (5 grams), heated on the steam-bath with a saturated aqueous solution of hydrobromic acid (5 grams), was mostly unaffected after two hours.

(*b*) Under similar conditions, but with 25 grams of the acid, complete hydrolysis was effected, with the production of nitrocatechol (m. p. 167°). (Found, C=46·5; H=3·3. Calc., C=46·4; H=3·2 per cent.)

(*c*) Nitroveratrole (5 grams) was heated on the steam-bath with saturated hydrobromic acid (15 c.c.) until a sample diluted with water was completely soluble in alkali. The liquid was diluted with water, and the precipitated nitroguaiacol crystallised twice from hot water. It was obtained in long, pale yellow needles, melting at 104—105°. Its acetyl derivative, prepared by the action of acetic anhydride and sodium acetate, melted at 101°, and was identical with the product obtained by the direct nitration of acetylguaiacol.

The identity of the nitroguaiacol and its acetate, obtained as described above, with the compounds from the nitration of acetylguaiacol, was proved by direct comparison and by the method of mixed melting points.

5-Nitroguaiacol dissolves in aqueous potassium hydroxide to an intense orange-red solution, which, when diluted with much water, never becomes pure yellow, a behaviour that affords a sharp qualitative distinction from the isomeric 4-nitroguaiacol.

It is interesting to note that 5-nitroguaiacol is the particular isomeride produced in the semi-methylation of nitrocatechol under the following conditions. The monopotassium salt of nitrocatechol was first prepared by dissolving the phenol (10 grams) in as little alcohol as possible, and adding potassium hydroxide (3·6 grams)

dissolved in the same solvent. The red, crystalline precipitate was collected and dried. The salt (4 grams) was heated with methyl iodide (4 grams) and ethyl alcohol (10 c.c.) in a sealed tube at 100° during several hours.

The product was extracted with ether, the ethereal solution washed, dried, evaporated, and the residue crystallised from water. The pale yellow needles melted at 103—104°, and the melting point was not depressed when the substance was mixed with undoubted 5-nitroguaiacol.

4-Nitroguaiacol (I).

We have prepared this compound by Rupe's method (*loc. cit.*), and identified it by careful comparison, as well as by the method of mixed melting points, with the nitroguaiacol obtained as follows.

Nitroveratrole (5 grams) was boiled under reflux with potassium hydroxide (10 grams), methyl alcohol (50 c.c.), and water (20 c.c.) during twelve hours. The unchanged nitroveratrole (2·8 grams) was removed by extraction with ether, and the orange aqueous solution separated, acidified, and again extracted with ether. The dried extract was evaporated, when the residue (2 grams) solidified, and was recrystallised from light petroleum (b. p. 50—60°) containing a little benzene. Pale yellow needles, melting at 101—102°, were obtained, and a mixture with 5-nitroguaiacol melted at 72—76°. 4-Nitroguaiacol dissolves in aqueous potassium hydroxide to an orange-yellow solution on dilution with water. Nitrocatechol is produced from 4-nitroguaiacol by hydrolysis with hydrobromic acid under conditions whereby nitroveratrole yields 5-nitroguaiacol and the latter compound remains unchanged.

*6-Nitro-4-hydroxy-*m*-tolyl Methyl Ether,*

6-Nitrohomoveratrole (10 grams) was heated on the steam-bath with glacial acetic acid (50 c.c.) and aqueous hydrobromic acid (50 grams, saturated at 0°) until a test portion dissolved completely in aqueous potassium hydroxide. The mixture was then diluted with water, and the greater part of the acid neutralised with potassium hydroxide.

The compound crystallised from the hot solution, and, after collection and recrystallisation from aqueous methyl alcohol, was obtained in bright yellow prisms, melting at 138—140°:

0·1249 gave 0·2413 CO_2 and 0·0563 H_2O. C=52·7; H=5·0.
$C_8H_9O_4N$ requires C=52·5; H=4·9 per cent.

The substance is readily soluble in most organic solvents and in alkali hydroxides to a red solution. The *potassium* salt crystallises from alcohol in slender, yellow needles. On treatment with nitric acid in glacial acetic acid solution, a colourless substance, probably a dinitro-compound, separated in prisms. The mother liquor from the separation of the 6-nitro-4-hydroxy-*m*-tolyl methyl ether was neutralised, using the nitrophenols it contains as indicator, and, after some time, a further crop of crystals, much smaller than the first, was deposited. After crystallisation from water, this product melted and decomposed at 180—182°, and since it also developed a green coloration with ferric chloride, it is certainly identical with the non-volatile nitrohomocatechol of Cousin (*Bull. Soc. chim.*, 1893, [iii], **9**, 53, 157).

Acetyl derivative.—4-Acetoxy-*m*-tolyl methyl ether was nitrated with twice its own weight of nitric acid in glacial acetic acid solution. The reaction was allowed to proceed, with careful cooling, during twelve hours, when the product was poured into water, and the precipitate collected. It crystallises from alcohol in pale yellow, feathery needles, melting at 138—139°:

0·1173 gave 0·2294 CO_2 and 0·0536 H_2O. C = 53·3; H = 5·1.
$C_{10}H_{11}O_5N$ requires C = 53·3; H = 4·9 per cent.

On treatment with alcoholic potassium hydroxide, and subsequent acidification, a nitrohydroxytolyl methyl ether was obtained which melted at 138—140°, and at the same temperature when mixed with the nitrohydroxytolyl methyl ether from the hydrolysis of 6-nitrohomoveratrole. The acetyl derivative was also prepared by the action of acetic anhydride on the potassium salt of 6-nitro-4-hydroxy-*m*-tolyl methyl ether, and found to melt at 138—139° alone or mixed with the substance obtained in the nitration of 4-acetoxy-*m*-tolyl methyl ether. It is strange that both 5-nitroguaiacol and 6-nitro-4-hydroxy-*m*-tolyl methyl ether melt at approximately the same temperatures as their acetyl derivatives.

THE UNIVERSITIES OF
MANCHESTER AND SYDNEY. [*Received, Feb. 2nd*, 1915.]

XXIX.—*Azotisation by Chloroamine.*

By Martin Onslow Forster.

Notwithstanding the numerous and protracted discussions which have centred in the diazo-group, the mechanism of the well-known experiment by which Griess first prepared phenylazoimide (diazobenzeneimide), namely, the action of ammonia on benzenediazonium perbromide, has never been explained. At the time of the discovery (*Annalen*, 1864, **137**, 65), Griess contented himself with the equation $C_6H_4N_2,HBr_3+4NH_3=C_6H_5N_3+3NH_4Br$, which has from time to time undergone the modifications necessary to conformity with the Kekulé formula and the Strecker-Blomstrand formula for diazonium salts, successively.

Apart from its historical interest, the experiment is important owing to its bearing on the constitution of the triazo-group, a question which is still unsettled, although the present tendency is to favour:

$$-N{:}N{:}N \quad \text{in preference to} \quad -N\!<\!\overset{N}{\underset{N}{\|}}.$$

This consideration, however, involves also the constitution of the diazonium perbromides, discussion of which has been summarised by Chattaway (T., 1909, **95**, 862), who claims for these compounds the structure of *N*-tribromohydrazines, $R{\cdot}NBr{\cdot}NBr_2$, in opposition to Hantzsch (*Ber.*, 1895, **28**, 2755), who advocates the diazonium perhaloid representation, $R{\cdot}NBr_3{:}N$.

It appears to me, however, that the foundation of Chattaway's claim is insecure. His objection to Hantzsch's formula, "that it immensely complicates" the formation of triazo-compounds by the action of ammonia, is without force until the azoimide nucleus is established as a cycloid, a conclusion which at present seems remote. His argument that "the view rejected by Kekulé and later adopted by Erlenmeyer, that the diazonium perbromides have the constitution $R{\cdot}NBr{\cdot}NBr_2$, that is, are *N*-tribromo-derivatives of the aromatic hydrazines, receives strong support from the fact that they are produced quantitatively when the requisite amounts of bromine are added to aromatic hydrazines dissolved in acetic acid" (*loc. cit.*, p. 863), collapses in face of his own experiment described in the previous year (T., 1908, **93**, 855), which showed quite clearly that if the amount of bromine employed is two-thirds of that required for the perbromide, the diazonium bromide is produced quantitatively, so that the experiment which gives such "strong support" to the *N*-tribromohydrazine formula is neither more nor less than adding one molecular proportion of bromine to the diazonium

bromide. Moreover, the probability that diazonium perbromide formation is due to the capacity of ionisable bromine to combine with more of the element is strongly indicated by a circumstance mentioned by Hantzsch (*loc. cit.*), namely, the failure of diazocyanides to form *N*-dibromocyanohydrazines with bromine, which even in less than one molecular proportion displaces the cyanogen group, and then forms the diazonium perbromide; this cogent point is not met by Chattaway.

A contribution to this question by Bülow and Schmachtenberg (*Ber.*, 1908, **41**, 2607) brings forward further evidence in favour of the perbromide formula. Not only do acetone and acetophenone, at 14·9°, convert the perbromide into diazonium bromide, with the liberation of hydrogen bromide and production of the corresponding bromo-ketone, but cinnamic acid, ethyl cinnamate, and phenylpropiolic acid are transformed into their respective dibromides, just as if they had been treated with the calculated amount of the free halogen. Chattaway does not refer to these experiments.

These remarks appear to me necessary because (1) hazy views regarding the diazonium perbromides must retard a just decision concerning the structure of azoimide, and (2) Chattaway's recent paper on ammonium perhaloids (this vol., p. 105) iterates his claim that "diazonium perhaloids are not perhaloids at all," and there is danger in accepting this statement without a close examination of the arguments upon which it is based. The statement may be true, but I venture to urge that it has not been proved.

It was not, however, from this point of view that the experiments described herein were conducted, but rather to ascertain the mechanism of azoimide formation from ammonia and diazonium perbromides. If the latter are really *N*-tribromohydrazines, there appears to be no alternative to the cycloid structure for triazocompounds. If, on the other hand, they are genuine perhaloids, two explanations are possible, one of which is as follows:

$$X\cdot\overset{\cdot\cdot}{N}\cdot Br,Br_2 + NH_3 = 3HBr + \left[X\cdot\overset{\cdot\cdot}{N}\cdot N\right],$$

$$\left[X\cdot\overset{\cdot\cdot}{N}\cdot N\right] \longrightarrow X\cdot N\!<\!\begin{matrix}N\\ \|\\ N\end{matrix} \quad \text{or} \quad X\cdot N{:}N{:}N.$$

The alternative depends on the production of bromoamine, which, although existing only momentarily, might yield a diazoaminocompound of such a type that excess of ammonia would convert it immediately into the arylazoimide by loss of hydrogen bromide:

$$X\cdot\overset{\cdot\cdot}{N}\cdot Br + NH_2Br = X\cdot N{:}N\cdot NHBr + HBr,$$

$$X\cdot N{:}N\cdot NHBr - HBr = X\cdot N{:}N{:}N.$$

Whilst it is not practicable to test this possibility with bromoamine itself, owing to its unstable character, the readiness with which chloroamine is available led me to study the action of this compound on the diazonium group, which I find is transformed by this agent into the triazo-nucleus; it is true that the yield is poor, but it is nevertheless sufficient to establish the reaction as a definite one. Since the chloroamine can be used only in the form of a solution produced by mixing sodium hypochlorite with ammonia, a system which also yields hydrazine, it was necessary to eliminate the possible effect of the last-named substance, because it is well known that aromatic azoimides are formed by the action of diazonium salts on hydrazine. Conditions were selected, therefore, in which hydrazine was absent from the solution, and the action of sodium hypochlorite alone on diazonium salts was found to proceed in a different direction.

It may thus be claimed that chloroamine behaves as an azotising agent, inasmuch as it converts a diazo-group into one containing three atoms of nitrogen. This power to add nitrogen by chloroamine has been applied also to the monoximes of α-diketones, which are transformed into the corresponding diazo-compounds, benzilmonoxime, for instance, yielding benzoylphenylazomethylene (diazodeoxybenzoin):

$$\begin{matrix} C_6H_5\cdot C{:}NOH \\ | \\ C_6H_5\cdot CO \end{matrix} + NH_2Cl = \begin{matrix} C_6H_5\cdot C{:}N_2 \\ | \\ C_6H_5\cdot CO \end{matrix} + H_2O + HCl.$$

In this type of action there has not been observed any pronounced difference between the two isomeric forms of the oxime, excepting that the proportion of benzonitrile which accompanies the diazo-compound appears to be somewhat greater from β-benziloxime (*anti*) than from the *syn*-modification.

Although the diazotisation of a quinonemonoxime has been extended to *iso*nitrosocamphor and *iso*nitrosoepicamphor, it has not been found applicable to *p*-nitrosophenol, neither has nitrosobenzene been converted into a diazonium salt by chloroamine; although empirically this would be possible, according to the equation:

$$C_6H_5\cdot NO + NH_2Cl = C_6H_5\cdot N_2Cl + H_2O,$$

it was nevertheless highly improbable, for whilst this formation of a diazonium salt would harmonise with the Kekulé formula, it is inconsistent with the Strecker-Blomstrand representation. The indifference of these two compounds would suggest that in alkaline solution *p*-nitrosophenol behaves as a true nitroso-compound rather than as the monoxime of *p*-benzoquinone, because the latter, from analogy to benzilmonoxime, *iso*nitrosocamphor, and *iso*nitrosoepicamphor, might certainly be expected to yield a diazo-compound.

It is perhaps not without significance that these examples of

azotisation by chloroamine, whether occurring with diazonium hydroxides or *iso*nitrosoketones, depend on a transformation of the group :NOH, and it is therefore reasonable to inquire whether the hydrazine equation should not be written as follows:

$$H_4N{\cdot}OH + H_2NCl = H_2O + HCl + H_4N{\cdot}N \longrightarrow H_2N{\cdot}NH_2,$$

rather than:

$$NH_3 + NH_2Cl = NH_2{\cdot}NH_2 + HCl,$$

as is commonly done. With this in view, and recalling the abnormal behaviour of aminocamphor (T., 1914, **105**, 2770), I have included piperidine among the materials investigated, seeing that either *N*-chloropiperidine or piperylhydrazine might be expected; it is the latter substance which is actually produced, thus bringing piperidine into line with ammonia.

Incidentally, it may be mentioned that although the production of azoimides herein described is not a useful method of preparation, the new process for obtaining diazocamphor is far superior in convenience to the existing ones, namely, action of nitrous acid on dihydrodicamphenepyrazine (Schiff, *Ber.*, 1881, **14**, 1375) and on aminocamphor (Angeli, *Gazzetta*, 1893, **23**, ii, 351), or by oxidising the hydrazones of camphorquinone with mercuric oxide or mercury acetamide (Forster and Zimmerli, T., 1910, **97**, 2171).

Experimental.

Action of Chloroamine on Diazonium Salts.

It has been the practice to diazotise the amine, treat with sodium carbonate until faintly alkaline, and then add the calculated amount of sodium hypochlorite solution, which, immediately beforehand, has been mixed with ammonia. Two examples will suffice.

Aniline.—A diazonium solution from 4·6 grams of aniline was neutralised with sodium carbonate, and, in the presence of much ice, treated with chloroamine freshly prepared by mixing 165 c.c. of sodium hypochlorite solution (containing 32 grams of available chlorine per litre) with 3 c.c. of ammonia (0·88) diluted to 25 c.c.; the liquid immediately became turbid, and the odour of chloroamine slowly faded, giving place to that of phenylazoimide. After twenty-four hours in ice, the oil was extracted with ether, and the aqueous portion found to be indifferent towards alkaline β-naphthol although still liberating iodine from potassium iodide; the residue from the ethereal extract was distilled in steam, which left some tar, and the oily distillate was collected with ether, washed with sodium hydroxide (which became deep brown), and then with dilute hydrochloric acid (which remained colourless). After being dried with calcium chloride, the ether left 4 grams on evaporation.

The specimen of phenylazoimide was far from being pure, however, and as this experiment had involved considerable excess of sodium hypochlorite in order to avoid the formation of hydrazine (165 c.c., instead of 120 c.c.), the operation was repeated with 9·3 grams of aniline and 200 c.c. (instead of 240 c.c.), but in this case only 3 grams of phenylazoimide arose, again impure. It seemed best, therefore, to determine the yield by preparing a solid derivative.

p-*Nitroaniline.*—The base (13·8 grams) was diazotised in hydrochloric acid (30 c.c.) and glacial acetic acid (20 c.c.), and the filtered solution rendered alkaline with sodium carbonate; on adding chloroamine from 150 c.c. of sodium hypochlorite and 3 c.c. of ammonia diluted to 25 c.c. the liquid became turbid, the odour of chloroamine vanished, and a bulky, brown solid separated. After three hours this was filtered, the liquid still containing a considerable proportion of diazonium salt, whilst the solid weighed 9 grams. It was extracted four times with hot alcohol, which left a small quantity of tar undissolved, more of which was deposited as the liquid cooled; the decanted alcohol was then diluted largely with water, 7 grams of pale brown material being precipitated. This was extracted with hot petroleum (b. p. 60—80°), which removed 4 grams of *p*-nitrophenylazoimide (m. p. 72°), and left a tarry specimen of the diazoamino-compound of *p*-nitroaniline.

In another experiment, using the same quantity of base and an amount of chloroamine (from 200 c.c. of sodium hypochlorite) sufficient to transform all the diazonium salt, 3·5 grams of *p*-nitrophenylazoimide were obtained, the proportion of tar being increased, and thus the yield even under the more favourable conditions amounts to only about 25 per cent. of the theoretical quantity. Perhaps this could be augmented by using a considerable excess of ammonia, and thus ensuring the absence of unaltered hypochlorite, which, in the circumstances described, is almost certainly present, and would transform a portion of the diazonium salt into the diazoamino-compound (see below); since azoimides are produced from diazonium salts by the action of hydrazine, however, it appeared desirable to avoid all risk of the last-named substance being present.

In order to be sure that in the foregoing experiments the production of azoimides was not due to hydrazine, a solution of chloroamine similar to that used in the experiment with diazotised aniline was shaken vigorously with 4 grams of benzaldehyde, but although the smell of both ingredients was rapidly reduced in strength, there was not any change in appearance; had hydrazine been present, the liquid would have become suddenly turbid, and there would have been a crystalline separation of benzalazine. In the course of a few

hours, when the odour of benzaldehyde was scarcely perceptible and the oil had sunk in the liquid, it was extracted with ether and dried with calcium chloride. The product is doubtless benzylidenechloroamine, $C_6H_5 \cdot CH{:}NCl$, the benzaldehyde analogue of methylenechloroamine, described by Cross, Bevan, and Bacon (T., 1910, **97**, 2404), and on evaporating the ethereal solution on a water-bath the residue decomposed violently, leaving benzonitrile and ammonium chloride without a trace of hydrazine.

Action of Sodium Hypochlorite on Diazonium Salts.

A solution of *p*-nitrobenzenediazonium chloride prepared from 13·8 grams of the base as already described was filtered, rendered alkaline with sodium carbonate, and, in the presence of much ice, treated with 250 c.c. of the sodium hypochlorite solution, which produced immediately a pale brown, granular precipitate; this was collected and washed until the filtrate was indifferent to alkaline β-naphthol. The product weighed 11 grams, and consisted of the diazoamino-compound. On repeating this experiment with diazotised aniline and *p*-bromoaniline, a precipitate was formed in each case, but became tarry during filtration and washing, so that it was not found possible to isolate the diazoamino-compound in crystalline form.

Action of Chloroamine on iso*Nitrosoketones.*

syn-iso*Nitrosocamphor* (m. p. 154°).—Ten grams of this material freed from the isomeride were dissolved in normal sodium hydroxide and in presence of crushed ice treated with chloroamine from 330 c.c. of sodium hypochlorite and 6 c.c. of ammonia diluted to 50 c.c.; effervescence took place, and the liquid became turbid although remaining yellow. After forty-eight hours the diazocamphor which had separated in yellow crystals (5 grams) was collected, a further quantity (0·5 gram) being recovered from the mother liquor by extraction with ether. On repeating this experiment with one-half the proportion of chloroamine there was less gas and only 3·5 grams of diazocamphor, the filtrate yielding about 3 grams of unchanged *iso*nitrosocamphor when saturated with carbon dioxide.

anti-iso*Nitrosocamphor* (m. p. 114°).—One gram of the freshly prepared unstable modification was dissolved in normal sodium hydroxide, well iced, and treated with chloroamine from 10 c.c. of hypochlorite and 1 c.c. of ammonia diluted to 10 c.c., when yellow crystals began to separate after about one hour, increasing to 0·25 gram in two days, a further 0·15 gram being extracted from the filtrate. Using larger proportions of sodium hypochlorite, the

yield of diazocamphor was diminished, and with considerable excess was reduced to nothing. Thus there appears to be no material difference in behaviour between the two isomerides, and as the separation of these is troublesome, it is better to use the Claisen mixture of the two, from which the most favourable conditions for the preparation of diazocamphor are as follows: Ten grams dissolved in normal sodium hydroxide are treated with crushed ice, and chloroamine from 150 c.c. of sodium hypochlorite and 15 c.c. of ammonia diluted to 100 c.c., yielding 6·5 grams of diazocamphor in the course of a few hours, ether extracting a further 0·5 gram from the filtrate. Thus the optimum conditions give 70 per cent. of the theoretical quantity, and the diazocamphor obtained in this way is a very good specimen, melting at 72° instead of 74°, without recrystallisation.

syn-iso*Nitrosoepicamphor* (m. p. 170°).—The treatment with chloroamine was carried out under the conditions prescribed for unstable *iso*nitrosocamphor, 0·9 gram yielding 0·6 gram of a bright yellow, camphor-like solid, which doubtless consists of diazoepicamphor; it is freely soluble in methyl or ethyl alcohol, acetone, petroleum, or ether, and melts at 111° to a clear liquid, which does not evolve gas until the temperature is raised. Owing to the interest attaching to derivatives of epicamphor, this material is being investigated further.

On repeating this experiment with other proportions, namely, 5 grams of *iso*nitrosoepicamphor, 165 c.c. of sodium hypochlorite and 4 c.c. of ammonia, the yellow colour of the solution was bleached; after twenty-four hours sodium sulphite was added until there was not any reaction with potassium iodide, and the liquid saturated with carbon dioxide. It remained clear, but sulphuric acid precipitated a very viscous material, from which camphoric acid was ultimately isolated.

anti-iso*Nitrosoepicamphor* (m. p. 137°).—The yield of diazoepicamphor was inferior to that obtained from the stable modification, only 0·2 gram being produced from 0·9 gram with 10 c.c. of hypochlorite and 1 c.c. of ammonia diluted to 10 c.c. Associated with it, and separated from it by insolubility in cold petroleum, was 0·2 gram of a colourless substance, which melted at 272° after recrystallisation from alcohol.

syn-*Benziloxime* (m. p. 138°).—One gram dissolved in normal sodium hydroxide and well iced was treated with chloroamine from 10 c.c. of sodium hypochlorite and 1 c.c. of ammonia diluted to 10 c.c. There was no effervescence, the yellow colour persisted, and a turbidity appeared, golden-yellow crystals of diazodeoxybenzoin accumulating during the next twelve hours in association with

benzonitrile. If the proportion of hypochlorite is increased, or that of the ammonia diminished, the condition of the diazo-compound is degraded by an increased amount of the oily nitrile, whilst the liquid, after removal of these two substances by ether, is found to contain benzoic acid.

anti-*Benziloxime* (m. p. 113°).—The experiments with this material were conducted in the same way and led to the same result, excepting that the separation of benzonitrile was more rapid and the proportion of diazo-compound correspondingly diminished.

Action of Chloroamine on Piperidine.

A solution of chloroamine from 15 c.c. of sodium hypochlorite and 3 c.c. of ammonia diluted to 39 c.c. was added to 1 gram of piperidine suspended in ice; after two hours, during which the odour of the base had distinctly changed, whilst that of the chloroamine had faded, enough sodium sulphite to reduce available chlorine was added, and the liquid shaken vigorously with 0·8 gram of benzaldehyde. After twenty-four hours the crystalline product, consisting of benzylidenepiperylhydrazone, was recrystallised twice from dilute alcohol, forming lustrous plates melting at 68°. Knorr, who prepared piperylhydrazine by reducing nitrosopiperidine (*Annalen*, 1884, **222**, 299), records 62—63° as the melting point of the benzylidene derivative.

In conclusion, I desire to express my thanks to the Managers of the Royal Institution for their courtesy in placing a laboratory at my disposal.

THE DAVY-FARADAY LABORATORY
OF THE ROYAL INSTITUTION, W. [*Received, Feb. 4th*, 1915.]

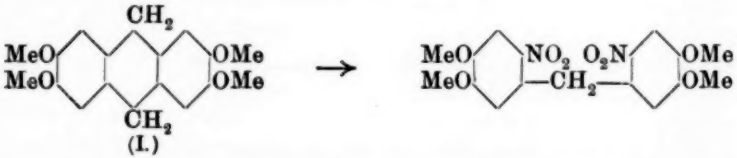
XXX.—*A Reaction of Homopiperonyl and of Homoveratryl Alcohols.*

By (MRS.) GERTRUDE MAUD ROBINSON.

DURING the course of an examination of the action of phosphorus pentachloride on methylenedioxy-compounds, Ewins (T., 1909, **95**, 1486) treated homopiperonyl alcohol with this reagent, and obtained a compound of high melting point and sparing solubility, which was regarded as dimethylenetetraoxydihydroanthracene (II), but direct proof was not available. Having had occasion to employ

homopiperonyl alcohol in connexion with synthetical researches, it was impossible to overlook the readiness with which this alcohol yields the substance obtained by Ewins, under the influence of mineral acids. Further, it was found that homoveratryl alcohol was readily condensed to an analogous substance by treatment, for example, with sulphuric acid in glacial acetic acid solution, and, on attempting to improve the method of preparation of homoveratryl alcohol by the employment of a process of condensation of veratrole and formaldehyde in the presence of 60 per cent. sulphuric acid, the condensation product of the alcohol was obtained in almost theoretical yield. A convenient process for the preparation of large quantities of this substance having been devised, it appeared desirable, in view of the intrinsic interest of the reaction, to make an investigation with the object of proving the constitution of the compound. The following observations show that the condensed homoveratryl alcohol is 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-*dihydroanthracene* (I). On distillation of the demethylated substance over zinc dust in a stream of hydrogen, 9 : 10-dihydroanthracene was obtained, whilst, on simultaneous oxidation and nitration by means of boiling 40 per cent. nitric acid, the condensation product yields 6-nitroveratric acid and 4 : 5-dinitroveratrole.

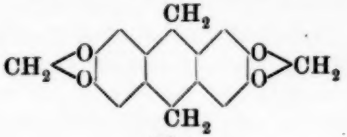
The latter result proves the orientation assumed in the formula to be correct, since no substances with substituents on the positions 3- or 6- of the veratrole ring can yield either of these products on treatment with nitric acid. Other reactions of the substance are described in the experimental portion of the paper, but the product of nitration deserves mention in this place. On treatment with nitric acid in acetic acid solution, the dihydroanthracene suffers fission in accordance with the scheme:



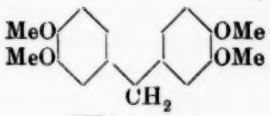
(I.)

The constitution of the product is proved by its production in the direct nitration of 3 : 4 : 3′ : 4′-*tetramethoxydiphenylmethane* (III), which was, in its turn, produced by the reduction of the corresponding tetramethoxybenzophenone by sodium and ethyl alcohol. This dinitro-derivative is either completely oxidised on boiling with nitric acid or is converted into a tetranitro-derivative of the diphenylmethane. It is really remarkable that oxidation of the methylene group to carbonyl does not occur simultaneously, but perhaps this is due to the influence of the nitro-groups on the distri-

bution of affinity in the molecule (compare Foulds and Robinson, T., 1914, **105**, 1964). This influence should strengthen the affinity between the carbon and hydrogen atoms of the methylene group, and so enable it to resist oxidation:

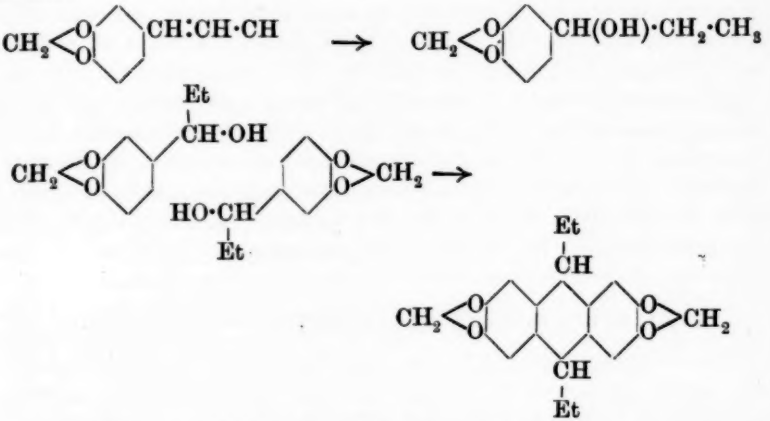


(II.)



(III.)

The extraordinary reactivity of homopiperonyl alcohol suggested that the polymerisation of *iso*safrole and similar processes may be due to a series of reactions which find expression in the following scheme:



If this theory were true there should be a *cis*- and a *trans*-form of such polymerides, and, indeed, in the case of di*iso*safrole, Angeli and Mola (*Gazzetta*, 1894, **24**, ii, 127) obtained a polymeride melting at 145°, whilst Puxeddu (*Gazzetta*, 1913, **43**, i, 128) produced a second dimeride of *iso*safrole melting at 95°. Mario Mayer (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 358) has cleared up much of the confusion existing in regard to these substances, and proves that the di*iso*safrole melting at 95° is converted by distillation into that melting at 145°. Both polymerides boil at 380°, and have identical absorption spectra in acetone solution. There is clearly already strong evidence that these substances are *cis-trans*-isomerides, and, in further support of the view enunciated in the above formulæ, it may be mentioned that di*iso*safrole may be produced from safrole by the use of a solution of sulphuric acid in acetic acid as the polymeriser. Judging from analogy it would seem that the isomeride melting at 145° is the *trans*-compound.

Experimental.

2:3:6:7-*Dimethylenetetraoxy*-9:10-*dihydroanthracene* (II).

This substance was obtained by Ewins (*loc. cit.*) by the action of phosphorus pentachloride on homopiperonyl alcohol, but the condensation occurs with very great facility, and can readily be accomplished by the use of the following conditions:

A solution of concentrated sulphuric acid (2 grams) in glacial acetic acid (20 c.c.) was gradually added to homopiperonyl alcohol (20 grams) dissolved in hot acetic acid (60 c.c.). The white solid which separated out almost at once was crystallised from nitrobenzene, and found to be identical with the compound prepared by Ewins' method. The very sparingly soluble anthracene derivative is sufficiently characteristic, but, to remove all doubt, the crystalline nitro-derivative was prepared by treatment with nitric acid in acetic acid solution, and found to melt at 217° in agreement with the experience of Ewins. In view of the experiments described in the ensuing sections there can be no doubt that the constitution of this compound is that of a dinitrodimethylenetetraoxydiphenylmethane, and the analyses that have been made confirm this conclusion (Found, C=51·9; H=2·9; N=8·2 [Ewins, *loc. cit.*]. $C_{15}H_{10}O_8N_2$ requires C=52·0; H=2·9; N=8·1 per cent.).

2:3:6:7-*Tetramethoxy*-9:10-*dihydroanthracene* (I).

This compound is readily produced by the action of acid condensing agents on homoveratryl alcohol, and was obtained by warming the alcohol (from the reduction of veratraldehyde by sodium amalgam in aqueous alcoholic solution) in glacial acetic acid containing a few drops of concentrated sulphuric acid, and the product was proved by the method of mixed melting points to be identical with that derived by application of the following very much more convenient process:

Veratrole (10 grams) was mixed with sulphuric acid (34 grams of 70 per cent.) and drop by drop with formaldehyde (14 grams of 35 per cent. aqueous solution), the whole being vigorously stirred and then allowed to remain during two hours at the room temperature.

A colourless solid separated from the rose-coloured mixture, and the substance could be obtained in a satisfactory condition by boiling the liquid after adding about 75 c.c. of alcohol and collecting the sparingly soluble, crystalline precipitate. The yield of the crude compound was almost equal to that demanded by theory.

The substance was recrystallised from benzene, and obtained in

long, colourless needles, which melt sharply and without decomposition at 227°:

0·1122 gave 0·2940 CO_2 and 0·0667 H_2O. C = 71·5; H = 6·6.

$C_{18}H_{20}O_4$ requires C = 72·0; H = 6·7 per cent.

The substance is very sparingly soluble in ether or alcohol, as well as in cold benzene, ethyl acetate, or acetic acid. It is soluble, however, in the last three solvents when hot, and crystallises from the solutions on cooling.

It dissolves in sulphuric acid to a rose solution, which rapidly becomes magenta, and on addition of water the colour disappears. On gently warming its solution in sulphuric acid, the colour changes to violet, and an almost black precipitate is obtained on the addition of water.

On boiling 10 grams of the tetramethoxydihydroanthracene with hydriodic acid (D 1·7; 35 grams) during half-an-hour, and pouring into water, a dark-coloured precipitate was obtained. This was collected, washed with sodium hydrogen sulphite solution, dried, and distilled in a stream of hydrogen over zinc dust in the usual manner.

In this way a product was obtained which solidified in contact with alcohol, and was crystallised from pyridine. It melted at 106°, and at the same temperature when mixed with a specimen of 9:10-dihydroanthracene prepared from anthraquinone by reduction with hydriodic acid and phosphorus in the way described by Liebermann and Topf (*Annalen*, 1882, **212**, 5).

Oxidation of the Hydroanthracene by Nitric Acid: Formation of 4:5-*Dinitroveratrole and* 6-*Nitroveratric Acid.*

Tetramethoxydihydroanthracene (4 grams) was boiled with nitric acid (50 c.c. of 40 per cent.) until a clear solution resulted, a condition achieved in about three hours. The liquid was rendered alkaline by means of sodium carbonate and extracted with chloroform; the solvent then removed from the extract by distillation, and the residue crystallised from water. The pale yellow needles so obtained were identified by direct comparison with 4:5-dinitroveratrole (m. p. 132°). The aqueous alkaline solution was rendered acid to Congo-red paper by means of hydrochloric acid and evaporated to dryness, the residue extracted with ether in a Soxhlet apparatus, the ether removed by distillation, and the remaining substance several times recrystallised from water. It melted at 187—188°, and was identified as 6-nitroveratric acid.

2:3:6:7-*Tetramethoxyanthracene*,

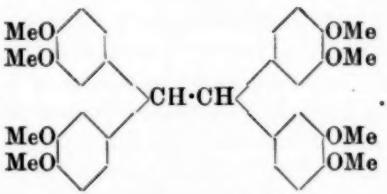
The removal of the two hydrogen atoms from the dihydro-derivative cannot readily be accomplished by any of the usual methods, and although the compound was ultimately obtained by the method described below, it could not be obtained in sufficient amount for a complete investigation.

Tetramethoxydihydroanthracene was mixed with a large excess of litharge and distilled from a hard glass flask. The yellow distillate solidified, and was found to be a mixture of unchanged substance and the anthracene derivative. The latter is very much more soluble in cold benzene than the former, and the crude product was accordingly digested with cold benzene, and the filtered yellow solution evaporated. The residue was crystallised from ethyl acetate, and obtained in very pale yellow prisms, which melted at about 141° with loss of solvent of crystallisation, re-solidified, and fused again at about 169°:

0·1165 gave 0·2926 CO_2 and 0·0686 H_2O. C = 68·5; H = 6·5.

$C_{18}H_{18}O_4,C_4H_8O_2$ requires C = 68·4; H = 6·7 per cent.

It thus appears that this anthracene derivative crystallises from ethyl acetate with one molecule of solvent of crystallisation. The crystals, on boiling with water, lost ethyl acetate, which was recognised by its odour. On crystallisation from alcohol the compound was obtained free from solvent of crystallisation, and melted at 173°. On account of the wastefulness of the process and the small yield obtained it was not deemed advisable to prepare sufficient of the material for analysis, as it is quite certain that the first specimen, the analysis of which is recorded above, really contained the solvent of crystallisation. The most characteristic property of the tetramethoxyanthracene is the brilliant blue fluorescence which its solutions in most solvents exhibit. In sulphuric acid solution it passes through the same colour changes as its dihydro-derivative.

s-*Tetraveratrylethane*, 

It was thought that the foregoing anthracene derivative might be produced (*a*) by condensing hydroveratroin internally, or (*b*) by the condensation of veratrole and glyoxal under suitable conditions.

A condensation product of hydroveratroin could be obtained by the use of tin tetrachloride, but it melted at 104°, and in this and other properties it resembled tetramethoxydeoxybenzoin (*Annalen*, 1903, **329**, 48). On the other hand, the condensation of glyoxal and veratrole in the presence of sulphuric acid led to the formation of the normal condensation product, that is to say, tetraveratrylethane. The experiment was carried out as follows: A mixture of veratrole (10 grams), glyoxal sodium hydrogen sulphite (10 grams), and sulphuric acid (34 grams of 70 per cent.) was shaken vigorously, and concentrated sulphuric acid (10 grams) gradually added. After the addition of the acid the mixture was warmed on the water-bath for ten minutes and then diluted with water. The solid which separated was collected and crystallised from benzene and then again from ethyl acetate. It was obtained in colourless needles, which melted at 148°:

0·1344 gave 0·3458 CO_2 and 0·0803 H_2O. C = 70·2; H = 6·6.

$C_{34}H_{38}O_8$ requires C = 71·0; H = 6·6 per cent.

The substance dissolves in sulphuric acid to a plum-coloured solution, which on the addition of water becomes first green and then pink.

3 : 4 : 3′ : 4′-*Tetramethoxydiphenylmethane* (III).

The starting point for the preparation of this diphenylmethane is the corresponding benzophenone, which was obtained by Kostanecki and Tambor (*Ber.*, 1906, **39**, 4027). Several points of simplification of procedure are, however, worthy of notice. Veratraldehyde is quantitatively oxidised to veratric acid by warm 2 per cent. aqueous potassium permanganate, and the product is at once obtained in the pure condition.

Then the acid yields the chloride by simply warming with one molecular proportion of phosphorus pentachloride, and after distilling away the phosphoryl chloride on a water-bath in a vacuum, the residue may be directly treated with aluminium chloride and veratrole in carbon disulphide solution. This reaction was carried out with only a gentle application of heat towards the end of the operation. After decomposition with ice-water, the mixture was distilled in a current of steam and the residue washed with ether, in which veratroylveratrole is very sparingly soluble, and crystallised from ethyl acetate. Veratraldehyde could in this series of processes be converted into more than its own weight of the final product.

Veratroylveratrole (17 grams) was dissolved as far as possible in 200 c.c. of boiling ethyl alcohol, and the solution treated with 22 grams of sodium cut in rather large pieces. The flask was heated

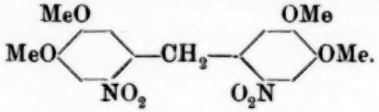
under reflux in an oil-bath and the temperature regulated from time to time, so that the reaction was always as vigorous as was consistent with the prevention of loss by frothing. When the mixture had been heated during two hours, and a certain quantity of sodium remained undissolved, water was added and the cooled solution extracted with ether, the ethereal solution washed with water, dried, and distilled finally in a vacuum. The greater part of the product distilled at 257°/24 mm., and the substance solidified on cooling and keeping. It could be crystallised from aqueous alcohol and again from light petroleum (b. p. 60—70°), and was obtained in colourless, glistening leaflets, melting at 70°:

0·1295 gave 0·3362 CO_2 and 0·0824 H_2O. C = 70·8; H = 7·1.
$C_{17}H_{20}O_4$ requires C = 70·8; H = 6·9 per cent.

The substance gives in sulphuric acid a magenta coloration, which might perhaps suggest contamination with the corresponding benzhydrol, but careful crystallisation does not remove this property to any degree, and it appears to be characteristic of the compound.

On treatment with concentrated sulphuric acid and formaldehyde followed by addition of water and collection of the dark precipitate, a product was obtained which, on crystallisation from benzene, yielded tetramethoxydihydroanthracene identical with the substance described above and melting at 227°.

6 : 6′-*Dinitro*-3 : 4 : 3′ : 4′-*tetramethoxydiphenylmethane*,



This substance is obtained by the following two methods:

(*a*) Tetramethoxydihydroanthracene (2 grams) was mixed with glacial acetic acid (15 c.c.) and nitric acid (D 1·42; 6 c.c.), and heated until a vigorous reaction occurred, which was then allowed to proceed without further application of heat. On the addition of water, yellow crystals separated, and these were collected and recrystallised several times from ethyl acetate, in which solvent the substance is sparingly soluble in the cold. The pale yellow needles melted at 183°:

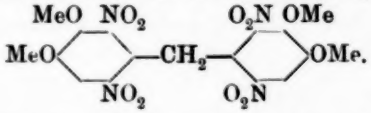
0·1162 gave 0·2306 CO_2 and 0·0516 H_2O. C = 54·1; H = 4·9.
$C_{17}H_{18}O_8N_2$ requires C = 54·0; H = 4·8 per cent.

For some at present inexplicable reason this compound does not give satisfactory values on estimating nitrogen by the direct method. The results obtained were always too high. The nature of the sub-

stance appears, however, to be established by the above analyses and also by the following method of preparation:

(*b*) Tetramethoxydiphenylmethane (see above) was dissolved in ten times its weight of glacial acetic acid and nitrated in the cold by the addition of twice its weight of ordinary concentrated nitric acid. After allowing to remain five minutes, the nitro-derivative was precipitated by water, collected, crystallised from ethyl acetate, and identified with the substance obtained as in (*a*) by direct comparison and the method of mixed melting points.

2 : 6 : 2′ : 6′-*Tetranitro*-3 : 4 : 3′ : 4′-*tetramethoxydiphenylmethane*,



The dinitro-derivative described in the previous section was dissolved in fifteen times its weight of nitric acid, and the solution boiled during two minutes, when a rather vigorous oxidation occurred and brown fumes were evolved. A solid, crystalline substance separated, however, and after addition of water this was collected and recrystallised from ethyl acetate. The sparingly soluble substance crystallised in almost colourless, rhombic prisms, melting at 210°:

0·1364 gave 0·2188 CO_2 and 0·0462 H_2O. C = 43·7; H = 3·7.

$C_{17}H_{16}O_{13}N_4$ requires C = 43·6; H = 3·4 per cent.

It is clear from this analysis that the methylene group of the substance has remained intact and unoxidised, and that the process is merely one of nitration accompanied by complete oxidation of a portion of the substance. In some experiments with fuming nitric acid a considerable amount of oxalic acid was obtained as the product of the reaction.

Di-iso*safrole*.

A mixture of *iso*safrole (10 grams), acetic acid (15 c.c.), and sulphuric acid (0·5 c.c.) was heated on the steam-bath during three hours. The product was diluted with water, and distilled in a current of steam to remove acetic acid and a small quantity of unchanged *iso*safrole. The polymeride remained as a viscid mass, and was separated as far as possible from the aqueous liquid and dissolved in the smallest possible amount of ethyl acetate. On the addition of alcohol just insufficient in amount to precipitate oily matter, and on keeping the liquid, a substance crystallised slowly, and was collected. This proved to be the di-*iso*safrole melting at 145°, and the compound gave that melting point after crystallisation

from glacial acetic acid. The larger amount of the polymerides remained in the solution, and may be distilled in a vacuum after removal of the solvent; the viscid oil boiled at 255°/30 mm. Mario Mayer (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 358) states that di-*iso*safrole melting at 92° yields the isomeride melting at 145° on distillation, but the oil obtained as above did not crystallise.

Unfortunately no crystalline nitro-derivative was obtained from this compound, although the experiments were conducted under the most varied conditions. On the other hand, there was always evidence of the production of a fatty acid higher in the series than acetic acid, and this acid is probably propionic acid, since it yields a sparingly soluble silver salt and a characteristic barium salt. The odour of the acid was also suggestive of propionic acid.

THE UNIVERSITY OF SYDNEY. [*Received, Feb. 2nd*, 1915.]

XXXI.—*The Dielectric Constants of Some Organic Solvents at their Melting or Boiling Points.*

By JOHN DOUGLAS CAUWOOD and WILLIAM ERNEST STEPHEN TURNER.

THE dielectric constant of a solvent has at various times been correlated with other of its physical properties, such as solvent power, degree of molecular complexity, and its power of producing ionisation or of permitting the formation of molecular aggregates by dissolved substances.

In all the comparisons of the dielectric constant with one of the physical properties mentioned, no attempt, so far as we are aware, has been made to carry them out at precisely the same temperature. The investigations which have been carried out and others still in progress in this laboratory on molecular complexity in solution have required for their satisfactory accomplishment a knowledge of the dielectric constants of solvents at either the melting or boiling point; and it was for the purpose of gaining this information that the measurements recorded below were made.

Previous investigations in which the effect of the variation of temperature on dielectric constant has been tested have been made by Cohn (*Ann. Physik*, 1892, [iv], **45**, 370); Heerwagen (*ibid.*, 1893, [iv], **48**, 35; **49**, 272); Franke (*ibid.*, 1893, [iv], **50**, 170); Thwing (*Zeitsch. physikal. Chem.*, 1894, **14**, 289); Rosa (*Phil. Mag.*, 1891, [v], **31**, 188); Palaz (*J. Phys.*, 1886, **5**, 370); Cassie (*Phil.*

Trans., 1890, [*A*], **181**, 1); Negreano (*Compt. rend.*, 1892, **114**, 345); Ratz (*Zeitsch. physikal. Chem.*, 1896, **19**, 94); Abegg and Seitz (*ibid.*, 1899, **29**, 242), and Walden (*ibid.*, 1910, **70**, 569). Of these, the most important measurements are by Ratz and by Walden; yet the range of temperature tested was in many cases so restricted that trustworthy values outside the range cannot be obtained by extrapolation. A few approximate values derived by extrapolation have been quoted in a previous communication (Turner and Pollard, T., 1914, **105**, 1751).

We now record values for the dielectric constant either at the melting or boiling point (or both) for benzene, naphthalene, and *cyclo*hexane; *o*- and *p*-chloronitrobenzene and *p*-dichlorobenzene; *p*-chloro-, bromo-, and iodo-toluenes and *p*-nitrotoluene; chloroform and bromoform; *p*-toluidine, diphenylamine, and pyridine; veratrole; benzil; *iso*amyl alcohol and dimethylethylcarbinol; methyl succinate and methyl *p*-toluate. In order to determine the values at the boiling point, measurements were made at a series of temperatures, and the value required was obtained graphically. The same method was adopted in one or two cases for the value at the melting point, but in others by a direct determination either at or within 1° of the melting point.

The bearing of the results on the molecular state of dissolved substances has already been discussed (Turner and Pollard, *loc. cit.*).

In regard to the effect of chemical constitution on the dielectric constant of a substance, there is little that is new brought to light. The great increase in the dielectric constant produced by the entry of a single nitro-group into a hydrocarbon or halogen derivative of a hydrocarbon is again shown, as illustrated by:

p-Nitrotoluene	$K_{52°} = 18{\cdot}44$	*p*-Chloronitrobenzene	$K_{83°} = 12{\cdot}7$
p-Chlorotoluene	$K_{30°} = 5{\cdot}85$	*p*-Dichlorobenzene ...	$K_{53} = 2{\cdot}82$

For halogen substitution the relative effect of chlorine, bromine, and iodine on toluene is different according as the halogen occupies the ortho- or the para-position:

Dobroserdov.*		Cauwood and Turner.	
o-Chlorotoluene	$K_{20°} = 4{\cdot}73$	*p*-Chlorotoluene	$K_{30°} = 5{\cdot}85$
m-Bromotoluene ...	$K_{20{\cdot}5°} = 5{\cdot}32$	*p*-Bromotoluene.....	$K_{28°} = 5{\cdot}07$
		p-Iodotoluene	$K_{35°} = 4{\cdot}40$

* *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 111.

Usually the chloro-derivative has the highest, and the iodo-derivative the lowest dielectric constant (compare Walden, *loc. cit.*).

A constitutive effect worth noting is the difference between the isomeric alcohols, *iso*amyl alcohol and dimethylethylcarbinol, which have values at 20° of 15·0 (obtained graphically) and 11·5, respec-

tively. When compared at their boiling points, this order is reversed.

The results of our measurements at different temperatures may be stated as follows:

(1) The decrease of dielectric constant with the temperature is either linear (chloroform, *cyclo*hexane, *p*-chlorotoluene, pyridine) or very nearly so. If the values of the dielectric constant are plotted as ordinates, and temperatures as abscissæ, the curve, when other than a straight line, is slightly sagged. Ratz found this curvature to be general. There is no evident relationship between the extent of curvature and the chemical character.

(2) The temperature-coefficient of dielectric constant of hydrocarbons is very small. Thus, for benzene it is 0·00066, and for *cyclo*hexane 0·00078, whereas for bromoform, which has the next lowest coefficient for the substances tested, it is 0·00255.

We had a special object in view in determining the dielectric constant of benzene over a range of temperature up to the boiling point. Innes (T., 1902, **81**, 682) used benzene in an investigation of the effect of the variation of temperature on the molecular weight of dissolved substances, but does not appear to have taken into account the fact that not only is molecular complexity affected by temperature, but also by the dielectric constant which is, in turn, influenced by temperature. Our results indicate, however, that the choice of benzene as solvent was a fortunate one, and that the effects Innes observed were due almost wholly to the variation of temperature.

(3) Among the substances investigated by us, the two alcohols, *iso*amyl alcohol and dimethylethylcarbinol, have the highest temperature-coefficients. Subsequent calculations made by us from the data of Abegg and Seitz and of Walden showed that no connexion exists between molecular complexity and temperature-coefficient of dielectric constant.

Experimental.

The method and apparatus followed closely those described by Nernst (*Zeitsch. physikal. Chem.*, 1894, **14**, 622), but the fixed liquid resistances were replaced, with considerable advantage, by two post-office boxes, each throwing 11,000 ohms resistance into the circuit as a rule.

In order to make measurements at different temperatures, the nickel cell (a crucible) containing the material was lowered into a weighted glass cylinder containing a deep layer of fused calcium chloride to desiccate the air in the cylinder. The latter was immersed in a thermostat to an extent sufficient to make the top of the cell about 7·5 cm. below the outside water-level.

The standard substance employed was benzene, the dielectric constant of which at 17° was found by Nernst to be 2·255. Unless otherwise stated below, benzene was employed as comparison substance and Nernst's value as standard.

In regard to the sensitiveness and sharpness of the minima some notes appear below, and, in addition, some observations on the effect of traces of impurity were made. Thus, sour samples of chloroform and bromoform gave better minima than the pure material. On the other hand, benzil improved in this respect with repeated crystallisation, impure material giving very flat minima. Benzene contaminated with ebonite (from the cap of the cell) through being heated too long at the higher temperatures gave minima quite as sharp as the pure benzene. The effect of the ebonite was to increase the dielectric constant.

In the tables below, the first column gives the temperatures at which determinations were made, the second the dielectric constant found, and the third the temperature-coefficient:

$$\frac{1}{K}\frac{dK}{dT} = \frac{K_{t_1} - K_{t_2}}{t_1 - t_2} \cdot \frac{2}{K_{t_1} + K_{t_2}}.$$

The values $K_{\text{m. p.}}$ and $K_{\text{b. p.}}$ are the values at the melting point and boiling point respectively, and have been obtained in some cases by direct measurement, in others by extrapolation from a curve.

Benzene.—Thoroughly dried over sodium wire, then fractionally frozen, followed by fractional distillation. B. p. 78·70—78·73°/735 mm.:

10°	2·267	
[17° (Nernst)	2·255]	
30°	2·227	0·00066
50°	2·199	
70°	2·179	
$K_{5·5°} = K_{\text{m.p}} =$	2·275	
$K_{80°} = K_{\text{b.p.}} =$	2·170	

Naphthalene.—Re-sublimed before use:

80·5° ..... 3·22 $= K_{\text{m.p.}}$

cyclo*Hexane.*—Dried and distilled. B. p. 68·5—69·0°/750 mm.:

5°	2·074	
20°	2·050	0·00078
30°	2·034	
$K_{4·5°} = K_{\text{m.p.}} =$	2·075	

o-*Chloronitrobenzene.*—Recrystallised from ethyl alcohol until of constant melting point (32·0°). The dielectric constant of this substance appears to be greatly influenced by traces of impurity. A specimen once crystallised from alcohol gave $K_{33} = 44·6$. After recrystallisation and drying for four days over phosphoric oxide the

melting point was 31·98 and $K_{33°} = 18·5$; a further crystallisation and similar drying for twelve days brought the melting point to 32·00° and $K_{33°} = 17·8$, the value later on confirmed.

Comparison substance employed, nitrobenzene, $K_{20·5°} = 35·5$ (Walden, *loc. cit.*). Compensating resistance necessary:

$K_{\text{m.p.}} = K_{33°} =$	17·8

p-*Chloronitrobenzene.*—Purified like the ortho-compound. M. p. 83·5°:

83·5°	12·7

p-*Dichlorobenzene.*—M. p. 52·1°:

53·0°	2·82

p-*Chlorotoluene.*—B. p. 158·5—159·5°/730 mm.:

10°	6·304	
20°	6·098	0·00373
30°	5·850	
$K_{7·4°} = K_{\text{m.p.}}$	6·35	

Dobroserdov (*loc. cit.*) found, for wave-lengths $\lambda = 60$ cm., $K_{19°} = 6·22$.

p-*Bromotoluene.*—M. p. 28°:

28°	5·07

p-*Iodotoluene.*—Repeatedly crystallised from ethyl alcohol. M. p. 35°. Compensating resistance necessary:

35°	4·40

p-*Nitrotoluene.*—M. p. 52°. Compensating resistance necessary. Comparison substance was *iso*amyl alcohol, $K_{20°} = 15·0$:

52°	18·44

Chloroform.—Purified as in previous investigations (compare Peddle and Turner, T., 1913, **103**, 1202). B. p. 60·94—60·96°/755 mm.:

20°	4·884	
40°	4·526	0·00398
58°	4·198	
$K_{\text{b.p.}} (= K_{61·2}) =$	4·13	

The various values found for the dielectric constant of chloroform vary somewhat, as evident from the following results at ordinary atmospheric temperature: $K_{15°} = 4·800$ (Ratz, *loc. cit.*); $K_{22°} = 5·14$ (Nernst, *loc. cit.*); $K_{17°} = 4·95$ (Drude, *Zeitsch. physikal. Chem.*, 1897, **23**, 305); $K_{18°} = 5·2$ (B. B. Turner, *ibid.*, 1900, **35**, 385)

Bromoform.—Well dried and fractionally frozen eight nes. M. p. 7·5°:

8°	4·58	
17°	4·47	0·00255

Values found by previous investigators are: $K_{17°}=4·43$ (Drude); $K_{20·7°}=4·51$ (B. B. Turner).

p-*Toluidine.*—Purified by repeated crystallisation from light petroleum until of constant melting point (43·7°). Compensating resistance necessary:

44°	5·40

Diphenylamine.—Purified like *p*-toluidine. M. p. 52°:

52°	3·30

Pyridine.—Sample used in previous research was again fractionated. B. p. 114·0—114·2°/746·5 mm. Compensating resistance necessary. Dobroserdov's value at 18·5° taken as standard. Minima very indistinct, and results therefore only approximate:

[18·5°	12·40]
50°	11·39
80°	10·62
$K_{b.p.}=$	9·5

Veratrole.—Purified like *p*-toluidine. M. p. 22·5°. Standard substance chloroform, $K_{20°}=4·88$:

22·5°	4·47

Benzil.—Repeatedly crystallised from ethyl alcohol. Standard substance chloroform. Compensating resistance necessary. Minima poor:

95°	4·14

iso*Amyl Alcohol.*—Purified as in earlier investigation (Turner and Pollard, T., 1914, **105**, 1770). B. p. 128·3—128·4°/749·2 mm. Compensating resistance necessary. Minima poor. From the work of Abegg and Seitz and of Ratz, the variation of the dielectric constant of this substance is known between −100° and +60°. Ratz's value at 60° was adopted as standard:

[60°	10·66]	
80°	8·872	0·00801
99°	7·431	
$K_{b.p.}=$	5·7	

Dimethylethylcarbinol.—B. p. 101·7—102·2°/759 mm. Standard substance bromoform:

20°	11·52	
50°	10·00	0·00454
80°	8·756	
$K_{b.p.}=$	7·9	

Methyl Succinate.—B. p. 191·5—191·9°/735·5 mm. Compensating resistance necessary. M. p. 19·5°:

19·5°	5·12

Methyl p-*Toluate*.—Own preparation:

33°	4·28

We desire to express our thanks to the Government Grant Committee of the Royal Society for a grant which covered the cost of the materials used in this investigation.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, SHEFFIELD. [*Received Feb. 5th*, 1915.]

XXXII.—*The Solubility of Carbon Dioxide in Water in the Presence of Starch.*

By ALEXANDER FINDLAY and OWEN RHYS HOWELL.

THE solubility of carbon dioxide in water in the presence of starch was determined by Findlay and Williams (T., 1913, **103**, 636) at pressures lower than atmospheric, and by Findlay and Creighton (T., 1910, **97**, 536) at pressures above that of the atmosphere. From these determinations it appeared that the solubility increases slightly and continuously as the pressure is increased. As this behaviour is different from that found in the case of other colloids it seemed advisable to re-determine this solubility.

The apparatus employed was the same as that previously used, but it has been found possible to improve its working and manipulation so as to increase the accuracy of the measurements. We believe the accuracy of the present determinations may be taken as not much less than 0·1 per cent. In the previous determinations the initial and final volume of the gas in the burette was read at different pressures, and the dead space correction which had to be introduced was rather large. In the present series of determinations the dead-space correction was eliminated by reducing the pressure on the gas in the burette and connecting capillary to atmospheric pressure after the absorption of the gas. The volume of gas was, therefore, always read at the same pressure. This reading can be done more accurately than the reading of pressure, and although readings of the pressure must also be made, errors in such readings have comparatively little influence on the final result. By working in this way, also, the calculation becomes simplified, the solubility being given by the expression:

$$\text{Solubility} = \frac{\left[(v_1 - v_2)\frac{P}{P+p-p'}\right] - V_1}{V_2},$$

where v_1 and v_2 are the initial and final volumes of gas in the burette, both measured under atmospheric pressure; V_1 the volume of the gas space in the absorption pipette, and V_2 the volume of the absorbing liquid; P the atmospheric pressure, p the increase of pressure or diminution of pressure as shown by the manometer, and p' the vapour pressure of the liquid in the absorption pipette.

As in the previous experiments, the temperature of absorption was 25°. The carbon dioxide was prepared by the action of pure hydrochloric acid on white marble which had been boiled with water under reduced pressure in order to free it from any occluded air.

In order better to furnish a comparison with the determinations of Findlay and Creighton at higher pressures, the present measurements were extended to pressures considerably above that of the atmosphere. In the tables below, pressures are stated in millimetres of mercury.

I. *Solubility in Water.*

Pressure	297·7	402·6	548·6	645·0	762·8	969·8
Solubility	0·824	0·824	0·824	0·824	0·824	0·825
Pressure	295·3	383·6	532·7	621·7	757·7	958·6
Solubility	0·824	0·823	0·824	0·824	0·824	0·824
Pressure	272·3	372·1	535·2	633·4	763·8	987·6
Solubility	0·823	0·824	0·824	0·824	0·824	0·824

The mean value of these and of the other determinations made is 0·824.

II. *Solubility in Starch Solutions.*

For these determinations soluble starch was employed. In order to ascertain whether the method of preparation of the solutions has any influence on the solubility of the carbon dioxide, the starch solutions were prepared in three different ways. The concentration was in each case 5 per cent., and the density of the solutions was 1·016.

(*a*) The starch was made into a paste with cold water, and boiling water then added. The resulting clear solution was freed from air by attaching the flask to a filter-pump and allowing the solution to boil under diminished pressure for a few minutes. It was then cooled rapidly in a stream of cold water. The following values of the solubility were obtained:

Pressure	275·2	365·3	518·3	605·0	751·8	910·8
Solubility	0·811	0·810	0·802	0·799	0·796	0·798
Pressure	288·4	378·7	534·4	620·3	761·7	992·9
Solubility	0·810	0·811	0·802	0·800	0·797	0·801

(*b*) The starch solution, prepared as before, was boiled for an hour under a reflux condenser, freed from air in the manner

described, and cooled rapidly under water. The following are the numbers obtained:

Pressure	280·0	368·8	540·8	639·2	760·8	985·0
Solubility	0·813	0·810	0·798	0·797	0·797	0·796
Pressure	276·2	369·6	539·6	629·2	759·6	984·6
Solubility	0·813	0·810	0·798	0·797	0·797	0·800
Pressure	262·3	358·4	528·7	618·7	747·8	969·2
Solubility	0·814	0·811	0·799	0·798	0·796	0·799

(*c*) The solution, prepared as before, was boiled under a reflux condenser for two hours, freed from air as before, and allowed to cool slowly in air overnight. The solubility was as follows:

Pressure	270·0	362·6	535·9	635·4	760·4	984·4
Solubility	0·812	0·804	0·799	0·797	0·796	0·800
Pressure	267·1	357·2	521·2	610·7	758·2	982·7
Solubility	0·811	0·804	0·798	0·798	0·797	0·800

(*d*) The solution was prepared as described under (*c*), but was boiled for five hours:

Pressure	274·1	365·5	529·7	620·6	758·7	973·7
Solubility	0·812	0·806	0·802	0·801	0·801	0·803

From the above results it will be seen that the solubility of carbon dioxide in the presence of starch is not appreciably affected by such variations as arise from differences in the method of preparation of the starch solutions, a fact which is of interest in view of the results obtained by Findlay and King (T., 1913, **103**, 1170; 1914, **105**, 1297) with regard to the influence of such variations on the rate of escape of carbon dioxide from supersaturated solutions in presence of starch. The latter property is much more sensitive to changes in the medium than is the solubility.

The above results also show conclusively that the solubility of the carbon dioxide passes through a minimum, and that starch, therefore, behaves, in respect of its influence on the solubility of carbon dioxide, like the other neutral colloids previously investigated.

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[*Received, Feb. 12th*, 1915].

XXXIII.—*The Velocity of Ionisation at Low Temperatures.*

By Alexander Robert Normand.

It is known that ionisation proceeds very rapidly at the ordinary temperature, but no direct estimation of the velocity of ionisation has as yet been attempted.

As most chemical processes are greatly retarded at low temperatures, it was suggested to the author by Professor Walker that it might be possible to observe and measure the velocity of ionisation by a method the principle of which is as follows:

A solution of a salt in ethyl alcohol is kept in a bath at about $-100°$ until its temperature and its conductivity become constant. An equal quantity of the solvent, cooled to the same temperature, is then quickly added to the solution, and the whole well stirred. The conductivity is read off at intervals.

If the additional ionisation due to dilution proceeded slowly enough at this low temperature the conductivity of the diluted solution would, immediately after mixing, be half the conductivity of the original solution, and would then gradually rise to the value of the conductivity of the solution at half the original concentration; and from a curve showing the variation of the conductivity with time, a measurement of the velocity of ionisation would be possible. As a result of the work it was found that at $-98°$ and even at $-118°$ ionisation is complete in less than three minutes, and from a study of the time-curves it is probable that ionisation is completed within one minute at the lower of these temperatures.

Since there is a difference in temperature of 130° between $-118°$ and ordinary room temperature, and if we assume from the rule that a rise of 10° doubles the velocity of a reaction, it follows that at the ordinary temperature ionisation is completed in (1 minute)/2^{13}, or in something less than 1/100th of a second. In all probability this estimate of the velocity is much too low, since the effect of 1° change in temperature becomes greater as the temperature diminishes.

Experimental.

I. *A Simple Low-temperature Bath.*

Most of the thermostats designed for low temperatures have pentane as the bath-liquid, the cooling being carried out by means of the evaporation of liquid air in a coil immersed in the pentane.

These all require very close attention, and besides being expensive do not give a constant temperature.

It was necessary for the purpose of this research to construct a thermostat which should give a temperature of about $-100°$ constant to a degree. It was thought that the use of a pure liquid and the corresponding solid might satisfy the required conditions. Methyl alcohol freezes at $-97·8°$, a temperature near enough to $-100°$ for the purpose.

The apparatus employed consisted of a small, silvered vacuum flask of 3·5 cm. internal diameter and 15 cm. in depth, and a hollow, pointed glass rod used as a stirrer. The methyl alcohol filled the vacuum flask to within 2·5 cm. of its brim. The liquid air was siphoned over into the alcohol in successive small quantities, and, being denser than the alcohol, evaporated in the body of the alcohol whilst sinking in it. The cooling thus proceeded rapidly until solid formed, which was denser than the liquid and sank in it. When the freezing point was nearly reached a solid cake was formed at the surface after every addition of liquid air. This was broken and pushed down into the liquid by means of the rod. By repeating this process until a fairly large quantity of the solid was formed, and stirring the mixture of solid and liquid, the bath was ready for use. The addition of small quantities of liquid air from time to time and occasional stirring maintained the temperature nearly constant.

After a little experience in its use this arrangement was found to be very satisfactory. In different experiments the limits of temperature as registered by a pentane thermometer (with 5 cm. of the pentane column above the level of the bath) were:

I.	−97·5	and	−98·9	for 120	minutes.
II.	−97·3	„	−98·1	„ 100	„
III.	−97·0	„	−97·8	„ 180	„
IV.	−97·5	„	−98·4	„ 200	„

The cold methyl alcohol, on keeping for some hours, absorbs water from the air, with consequent lowering of the equilibrium temperature, which is no longer so easy to maintain constant. It is advisable, therefore, to use fresh alcohol for each experiment, or to allow the vacuum flask to attain room-temperature in a bell-jar desiccator.

Ethyl alcohol (f. p. $-117·6°$) was also used as a thermostat liquid; it is, however, not so useful, as near its freezing point it becomes very viscous and is difficult to stir.

Other liquids with different freezing points may be used in a similar way.

II. *Variation of Conductivity with Temperature.*

Advantage was taken of the conductivity apparatus described in the next section to obtain a curve showing the variation of conductivity with temperature of a solution of potassium iodide (1·055 grams) in ethyl alcohol (100 grams) between the limits $-100°$ and $+25°$.

Three test-tubes (15 cm. × 1·2 cm.) were used, two of these being arranged as electrolytic cells; in the third was placed the pentane thermometer previously mentioned and a quantity of solution. The three test-tubes were arranged symmetrically in a vacuum flask, the thermostat arrangement being that previously described. It was found that the time required for the contents of the vacuum vessel to rise in temperature from $-100°$ to $+5°$ was about eighteen hours, and it was assumed that the pentane thermometer immersed in tube 3 gave at any moment a fairly accurate approximation to the temperature of the solutions in the other two tubes.

Alongside the three tubes was placed a stoppered graduated tube of ordinary 5 mm. glass tubing containing a quantity of solution. The volume-readings of this tube were taken as giving the volume of the solution at successive temperatures.

The specific conductivity of the solvent alcohol was $0·86 \times 10^{-6}$ at 25°. At temperatures from $-100°$ to $-80°$ the alcohol with the apparatus used gave no measurable conductivity, and is thus negligible in comparison with the specific conductivities found for the potassium iodide solution at the various temperatures.

The figures obtained were:

Temperature.	Specific conductivity.	Volume.	Temperature.	Specific conductivity.	Volume.
−101·0°	$25·9 \times 10^{-6}$	—	−43·5°	$261·7 \times 10^{-6}$	63·5
−95·0	32·7	61·0	−37·9	311·0	64·0
−89·5	42·5	61·5	−30·1	386·8	64·5
−84·1	55·0	62·0	−23·0	469·8	65·0
−79·9	67·1	62·0	−19·0	521·4	65·0
−74·2	85·9	62·5	−15·2	571·6	65·0
−70·0	101·6	62·5	−10·0	648·3	65·0
−62·5	136·5	63·0	−4·0	746·9	65·5
−60·5	147·7	63·0	+0·1	827·0	66·0
−55·2	178·9	63·5	+8·8	981·9	66·2
−49·2	219·3	63·5	+24·9	1288·0	—

From these the following values for a solution of 1 gram of potassium iodide in 100 grams of alcohol have been calculated:

Temperature.	Specific conductivity.	Volume.	Temperature.	Specific conductivity.	Volume.
−100°	$25·7 \times 10^{-6}$	60·7	−40°	277×10^{-6}	63·9
−90	39·5	61·3	−30	367	64·4
−80	64	61·8	−20	483	64·9
−70	97	62·3	−10	614	65·5
−60	143	62·9	0	778	66·0
−50	204	63·4	+25	1223	67·8

It is noticeable that the temperature-coefficient of the conductivity is considerably greater at the lower than at the higher temperatures.

III. *Velocity of Ionisation.*

A solution of potassium iodide in ethyl alcohol was chosen because ethyl alcohol freezes at a lower temperature than methyl alcohol, the bath liquid, and because the variation of molecular conductivity (and therefore of ionisation) on doubling the dilution is favourable, potassium iodide being about half ionised in ethyl-alcoholic solution nearly saturated at $-100°$.

It was necessary to operate with a solution which should remain unsaturated at the temperature of freezing methyl alcohol. A saturated solution of potassium iodide in absolute alcohol was therefore prepared at this temperature and its concentration determined. The results obtained were as follows:

I.	100 grams of alcohol dissolved				1·134	grams of potassium iodide at				$-98°$
II.	"	"	"	"	1·142	"	"	"	"	"
III.	"	"	"	"	1·139	"	"	"	"	"
					Mean 1·138					

A solution of 1·055 grams of potassium iodide in 100 grams of alcohol was then prepared, which corresponds approximately with a $N/20$-solution at room temperature.

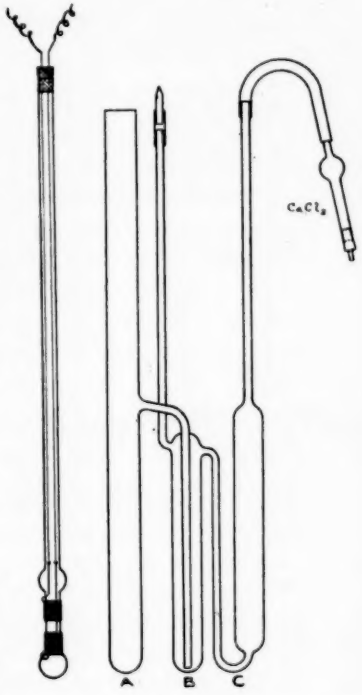
It was necessary to construct a cell which should permit of the addition of the pure solvent, maintained at the temperature of the bath, to the solution, and of mixing the resulting solution as rapidly as possible.

The form of cell finally adopted is shown in the figure. The electrodes and solution were placed in *A* and an equal volume of solvent in *B*. The apparatus was then placed in the thermostat (a bath of freezing methyl alcohol). When the conductivity of the solution in *A* reached a constant value, the solvent in *B* was blown over into *A*. The pipette *C* was added to ensure that as far as possible only cold air should come in contact with the solutions. Mixing was carried out by raising and lowering the electrode piece, which was provided with a bulb that nearly fitted the tube *A*.

The conductivities were determined by a modification of the rotating commutator method described by Whetham (*Phil. Trans.*, 1900, [*A*], **194**, 330). It was found that at low temperatures the most satisfactory results were obtained when the electrodes were platinised and then "greyed" by heating to redness for a short time. The galvanometer used was a unipivot dial instrument,

which was found to be very suitable for the rapid determination of a changing conductivity.

The results at first obtained from both forms of cell seemed to show that ionisation was proceeding with measurable slowness, but this was afterwards found to be the result of imperfect mixing, the increase of conductivity which was observed being probably due to the alteration in the concentration of the solution around the electrodes. Ethyl alcohol and solutions made from it become viscous at temperatures below $-90°$. Much stirring was therefore needed to produce a homogeneous solution when the alcohol was added to the potassium iodide solution. Sufficient stirring (100 strokes) could, however, be completed in less than a minute.



Blank experiments showed that the temporary disturbance caused by mixing and stirring—in the case of the cell described an increase of the conductivity, which then diminished to the constant value—disappeared in two or at most three minutes from the time the operation of mixing and stirring commenced.

Apart from this temporary disturbance, no indication could be observed that any change of conductivity, which could be attributed to a gradual increase of ionisation, was proceeding in the diluted solution; for example, the conductivity in one instance fell from the original reading of 185 to 111·5 within one minute of the time of dilution with an equal volume of alcohol, remaining thereafter constant at 110·5. There was thus no indication of a fall to $185 \div 2 = 92{\cdot}5$ due to mere dilution, and a subsequent increase to 110·5 due to increased ionisation.

The experiment was repeated at the temperature of freezing ethyl alcohol, namely, $-117{\cdot}6°$, the solvent in this case being an equimolecular mixture of methyl and ethyl alcohols.

The solution used was an approximately 1 per cent. solution of potassium iodide in the above alcohol mixture. Here also an

exactly similar result was obtained, the conductivity obtained on dilution remaining constant apart from the initial temporary disturbance.

The equimolecular mixture of ethyl and methyl alcohol behaves like a glass, having no definite freezing point. If a test-tube containing the mixture of alcohols is immersed in liquid air the volume is seen to diminish most markedly; at about $-130°$ the mixture becomes very viscous, and at about $-150°$ it is a hard solid which adheres to glass. On further cooling the volume continues to diminish noticeably, and unless the test-tube is cooled by very gradual immersion in the liquid air the whole mass cracks violently into small fragments.

The author has to thank Professor Walker, not only for the line of inquiry suggested, but for advice and encouragement received during the progress of the work, which was carried out in the Chemistry Department of the University of Edinburgh.

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[*Received Dec. 22nd*, 1914].

XXXIV.—*The Firing of Gases by Adiabatic Compression. Part III. The Ignition-points of Mixtures of Electrolytic Gas with Argon. Ratio of the Specific Heat for Nitrogen and Hydrogen.*

By James Murray Crofts.

An apparatus for the adiabatic compression of gases has been described by Dixon and Crofts (T., 1914, **105**, 2036), and an account was there given of experiments performed to determine the ignition-points of explosive mixtures of the type $2H_2+O_2$, $2H_2+O_2+xO_2$, $2H_2+O_2+xH_2$, $2H_2+O_2+xN_2$.

The ignition-points were calculated by means of the formula $\frac{T_2}{T_1} = \left[\frac{V_1}{V_2}\right]^{\gamma-1}$, where V_1 and V_2 denote the initial and final volumes of the compressed gases, T_1 and T_2 the initial and final temperatures of the gases on the absolute scale, and γ the ratio of the specific heat of a gas at constant pressure to that at constant volume. All the gases used were diatomic, and for γ the value 1·4 was taken $\left(\gamma=\frac{C_p}{C_v}=\frac{7}{5}=1{\cdot}4\right)$ as being a round figure, which was not only con-

venient, but also probable as the mean value between room temperature and 550°.

The addition of hydrogen and of nitrogen to electrolytic gas was shown to increase the ignition-temperature of the mixture, the increase being proportional to the amount of gas added.

It was felt that interesting results might be obtained if the ignition-points of the hydrogen and nitrogen mixtures were compared with corresponding mixtures with argon, and the present series of experiments was therefore undertaken. The advantage of using argon lies not only in the fact that it is an inert gas, but that it is monatomic, and therefore no change in its specific heats under alterations of temperature and pressure is to be apprehended. When the experiments had been performed—and it is to be noted that those given are a few only, typical of a very large number which were necessary definitely to establish the data—the ignition-points were calculated on the assumption that the molecular heats at constant volume (C_v) were 5·0 and 3·0 for the diatomic gases and argon respectively, and the corresponding values for the ratio γ of the specific heat at constant pressure to that at constant volume, 1·4 and 1·666 respectively. The ignition-points, obtained by means of calculations similar to that on page 297, showed that volumes of argon added to electrolytic gas produced a rise in the ignition-point proportional to the amount of gas added. In this respect the effect of argon is similar to that of nitrogen or hydrogen, although the amount of the increase of the temperature of ignition varied with the different gases.

It is obvious from the method of calculation that the figures given for these ignition-points depend on the value that is assigned to γ, and, in the case of mixtures of gases of different degrees of complexity, on the value given to C_v, and before proceeding further it will be as well to consider the existing experimental evidence.

The Effect of Changes of Temperature and of Pressure on Specific Heats.

The specific heat at constant volume for argon is a constant quantity under all conditions, as has been shown experimentally by Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536), but the specific heat of diatomic and more complex gases varies with the conditions of temperature and pressure. It has been found that the specific heat of such gases increases and the value of the ratio γ falls with rise of temperature, and references have been given in Part II. to the original papers; the effect of pressure has not been so thoroughly investigated, hence a summary of the principal work on the question may be given.

The greater number of investigations has concerned the changes in the specific heat at constant pressure. Lussana (*Nuovo Cim.*, 1894, [iii], **36**, 5, 70, 130) for hydrogen, air, and carbon dioxide, Witkowski (*J. Phys.*, 1896, [iii], **5**, 123), and Holborn and Jakob (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 213) for air, find in each case an increase in the value.

Few determinations of the alterations produced by pressure in specific heat at constant volume have been made. Joly (*Proc. Roy. Soc.*, 1894, **55**, 390) finds an increase in the value in the case of carbon dioxide and air, although the increase is not great in the latter case, and a slight decrease in the case of hydrogen. In the case of carbon dioxide above a certain density, increase of temperature results in a lowering of the value of C_v.

For the effect of pressure on the ratio of the specific heats, we have Amagat (*Compt. rend.*, 1895, **121**, 862) and Thibaut (*Ann. Physik*, 1911, [iv], **35**, 373) on carbon dioxide, and Koch (*Abh. d. Bayer. Akad. Wiss.*, 1907, **23**, 377) on air, in each case giving an increase of the ratio with rise of pressure. At high pressures, however, Koch obtained a diminution of the value with increased pressure. Valentiner (*Sitzungsber. K. Akad. München*, 1903, 691) working with nitrogen at low temperature also observes a rise in the value of γ with rise of pressure.

Some results have been obtained for the value of γ when both temperature and pressure are subject to alteration. Witkowski (*Bull. Acad. Sci. Cracow*, 1899, 138), Koch (*loc. cit.*), Lussana (*loc. cit.*), and others have shown that over various intervals of temperature and with various concomitant increases of pressure the value of γ increases for air and for carbon dioxide, but that the effects of pressure and of temperature are opposed to one another. The temperatures and pressures under which the experiments were conducted, however, do not correspond with the conditions of the experiments described in this paper. Later Worthing (*Phys. Rev.*, 1911, **33**, 217) has combined the results of other observers to obtain a value for γ, and has also given the results of some of his own experiments in which he used Manoeuvrier's modification of the method of Clément and Desormes. Some of the figures may be quoted: for air at 0° and 20 atmospheres' pressure, $\gamma = 1{\cdot}460$; with the same pressure but at $-79{\cdot}3°$, $\gamma = 1{\cdot}530$; whilst at 50 atmospheres' pressure the values are 1·533 and 1·767 respectively. These figures are derived from data obtained by Witkowski and by Koch by indirect methods. For carbon dioxide at a pressure of 28·52 atmospheres he gives from his own data:

Temperature	0·2°	31°	50°	98·5°
Value of γ	1·702	1·499	1·448	1 327

It would seem that if the temperature were raised beyond that last quoted, namely, 98·5°, the value of γ at the pressure of 28·52 atmospheres—which is a pressure met with in the present experiments—would gradually approach the value at normal temperature and pressure.

The experiments that were performed under conditions to some extent similar to those under which the present experiments were conducted are those on the specific heat at constant volume by the method first applied by Mallard and Le Chatelier (*Ann. des Mines*, 1884, **4**, 378). Here a gaseous mixture is exploded, and the pressure produced by the explosion measured. Then by the ordinary gas equations the maximum temperature attained by the gases can be calculated, and hence values for C_v found. Langen (*Mitteilungen über Forschungsarbeiten auf den Gebiete des Ingenieurwesen*, 1903, 8) improved on the method, and later still Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536; 1910, **16**, 897) has introduced still further modifications. In the explosion bomb very high temperatures are momentarily attained, and at the same time the pressure increases rapidly, although not nearly to such an extent as with gases adiabatically compressed. Notwithstanding the changes of pressure, however, Pier's results for the high temperatures agree very well with those which Holborn and Henning (*Ann. Physik*, 1907, [iv], **23**, 809) found for temperatures usually up to 800°, but at the ordinary pressure. Holborn and Henning's investigations concerned the value of C_p, but if the constant 1·985 is subtracted from them they agree well with those found by Pier for C_v.

In the Reports of the Committee appointed by the British Association to investigate the subject of gaseous explosions, some interesting references are made to the value of the specific heat of air and of carbon dioxide under adiabatic compression. Unfortunately, however, no detailed accounts of the experiments made appear to have been published. Clerk (*Brit. Assoc. Reports*, 1909, 250) is stated to have compressed repeatedly a volume of air, and, by means of the diagram of compression, he deduces a value of C_v for air = 5·28, at a mean temperature of 170°; this value, he observes, is in agreement with that found by extrapolation from Swann's figure (*Phil. Trans.*, 1910, [*A*], **210**, 199) for C_p, which was obtained by Regnault's method. For C_p at 170° Swann's results give 7·1, giving $C_v = 5·1$ or thereabouts. Hopkinson (*ibid.*, p. 253) compressed air in a gas engine and took a fresh charge at each compression; the final temperature attained was measured by means of a platinum resistance thermometer. He assumed that γ remained constant, and hence deduced a value for C_v which again is in close accord with that deduced from Swann's results.

One may then sum up the present knowledge regarding the values of C_v and γ for gases—C_p does not concern the calculations given in this paper—by saying that C_v increases, although only slightly, with rise of temperature and with rise of pressure for diatomic gases (except in the case of hydrogen, where there is probably a slight decrease); this value appears to reach a maximum at a point which depends on the compressibility of the gas; beyond this both increase of pressure and increase of temperature cause a diminution in the value of C_v. For γ the value increases with the pressure, but diminishes with the temperature.

Although no observations have been made on the changes in C_v and γ with simultaneous variations of temperature and pressure such as occur in a gas adiabatically compressed, it seems probable from the work already quoted that the variations in the magnitude are of no great amount, but it is evident that there is little to guide one in fixing on any particular value. Hence Dixon and Crofts selected 1·4 as the value of γ mainly for convenience.

In considering the ignition-points calculated by the use of arbitrary values of γ it is found that the addition of argon, hydrogen, or nitrogen to electrolytic gas raises the temperature at which explosion takes place in amounts which are proportional to the volume of gas added; the same effect is produced by the addition of carbon dioxide to electrolytic gas (see Part IV), and of argon, nitrogen, and carbon dioxide to the mixture $2CO + O_2$ (results to be published shortly). Now we know that argon must act as an inert gas, and both theoretical considerations and experimental evidence point to the excess of hydrogen and the added nitrogen behaving in a similar manner in the explosion of the electrolytic-gas mixtures. If this is so it follows that similarly constituted mixtures have the same ignition-temperatures; for example, the mixtures $2H_2 + O_2 + H_2$ and $2H_2 + O_2 + N_2$ must explode at the same temperature as the mixture $2H_2 + O_2 + A$. It is this assumption—which does not in itself appear rash, and is justified by the agreement of the results to which it leads—that is the basis of the calculations in this paper.

The first problem, therefore, is to fix the ignition-points of the mixtures $2H_2 + O_2 + xA$, and to do this it is essential to obtain values of γ and C_v for the electrolytic-gas portion of the mixture. It is shown below how such values can be obtained from the experimental data themselves, but before proceeding to this it is necessary to make clear the relations which are assumed to exist between C_p, C_v, and γ for the gases under the conditions of temperature and pressure which obtain in the actual experiments. Dixon and Crofts (*loc. cit.*) have shown that alterations in the initial tempera-

ture and pressure make no material difference to the ignition-point (obtained by the adiabatic method) of electrolytic gas, although the final pressure is altered considerably; it must follow, therefore, that under the conditions of the experiment the value of γ is not altered by changes of pressure. This result is in accordance with the fact already mentioned that values for C_v obtained by the explosion method of Mallard and Le Chatelier agree with those obtained for C_p by the mixture method of Regnault, using the most recent figures—those of Holborn and Henning—on subtracting from the latter the constant 1·985. In Mallard and Le Chatelier's method there are large changes of pressure; in Regnault's method there are none. The relation $C_p - C_v = 1{\cdot}985$ has, therefore, been employed in all the calculations.

To obtain a Value of γ for Electrolytic Gas.

The mixture $2H_2 + O_2 + A$ explodes when $V_2 = 38{\cdot}4$ and $T_1 = 286°$, $V_1 = 377$, as in all experiments; the mixture $2H_2 + O_2 + H_2$ explodes when $V_2 = 27{\cdot}6$ and $T_1 = 287{\cdot}2$. These mixtures, as explained above, may be taken to have the same ignition point; further, the final pressures in the two mixtures do not differ greatly (roughly a mean of 15 atmospheres in the argon mixture and 19 atmospheres in the other); in other words, the changes in temperature and pressure in the two mixtures when compressed adiabatically to the explosion point must approximate very closely.

It is known that the diatomic gases hydrogen, oxygen, and nitrogen have specific heats which differ ilttle from one another, and, so far as previous experiments go, show similar small variations under like changes of temperature and pressure (Pier, *loc. cit.*). The practical value for γ for the mixture $2H_2 + O_2 + H_2$ will, therefore, differ little from the practical value of γ for electrolytic gas, $2H_2 + O_2$, alone. Taking the argon mixture, let T_θ be the calorific mean between T_E, the temperature which would be produced by the given compression applied to electrolytic gas alone, and T_A the temperature similarly produced by compression of argon alone; and let x = the specific heat at constant volume of electrolytic gas, then for the mixture $2H_2 + O_2 + A$ we have by the method of mixtures:

$$3 \times x(T_\theta - T'_E) = 2{\cdot}981(T'_A - T'_\theta) \quad . \quad . \quad . \quad . \quad (1)$$

the figure 2·981 on the right-hand side of the equation represents C_v for argon, the figure 3 on the left-hand side corresponds with the three volumes of electrolytic gas in the given mixture. Now T_A is given by the experiment as $286\left[\frac{377}{38{\cdot}4}\right]^{\gamma-1}$ or $286\left[\frac{377}{38{\cdot}4}\right]^{0{\cdot}666}$; and T_θ is the ignition-point of the argon mixture, which is the same

as the ignition-point of the hydrogen mixture $2H_2+O_2+H_2$. Now the latter mixture explodes at $287\left[\frac{377}{27{\cdot}6}\right]^{\gamma-1}$ according to experiment, and $(\gamma-1)=\frac{1{\cdot}985}{C_v}$ or $\frac{1{\cdot}985}{x}$.

$$\therefore\ T_\theta = 287\left[\frac{377}{27{\cdot}6}\right]^{\frac{1{\cdot}985}{x}}.$$

T_x similarly is given by $286\left[\frac{377}{38{\cdot}4}\right]^{\frac{1{\cdot}985}{x}}$. Substituting these values of T_A, T_x and T_θ in equation (1) and we have:

$$3\times x\left[287\left(\frac{377}{27{\cdot}6}\right)^{\frac{1{\cdot}985}{x}}-286\left(\frac{377}{38{\cdot}4}\right)^{\frac{1{\cdot}985}{x}}\right]=$$
$$2\,981\left[286\left(\frac{377}{38{\cdot}5}\right)^{0{\cdot}666}-287\left(\frac{377}{27{\cdot}6}\right)^{\frac{1{\cdot}985}{x}}\right].$$

This equation contains but one unknown. By trial and error x is found to equal 5·01, that is, for electrolytic gas $C_v=5{\cdot}01$, and hence $\gamma=\frac{C_p}{C_v}=\frac{5{\cdot}01-1{\cdot}985}{5{\cdot}01}=1{\cdot}396$.

These values have been obtained from the experimental data alone, on the assumptions set out on page 294, which certainly are not outside the regions of probability. Further, the assumptions receive justification from the fact that calculations based on the figures so obtained give, as the ignition-points of mixtures $2H_2+O_2+A_x$, values which, on plotting, give a straight-line graph. These values for C_v and γ are the mean of the values at the beginning and at the end of the compression.

It is interesting to compare the value for C_v with that of other observers. Lewis and Randall (*J. Amer. Chem. Soc.*, 1913, **34**, 1128), in summing up the various determinations of C_p for hydrogen and oxygen, draw the conclusion that the most likely values for C_v are given by the equations:

$$C_v \text{ hydrogen}=4{\cdot}5+0{\cdot}001T.$$
$$C_v \text{ oxygen}\ =4{\cdot}5+0{\cdot}009T.$$

For the mixture $2H_2+O_2$ between 287° abs. (14°) and 803° abs. (520°) the mean $C_v=5{\cdot}008$, a value practically identical with that of 5·01 found as a result of the present experiments, although the equation of Lewis and Randall takes no account of alterations in C_v produced by change of pressure.

In all the calculations concerned with electrolytic gas the values found from Lewis and Randall's equations for hydrogen and oxygen have been used on account of the remarkable agreement between the value obtained by their use and the experimental value as

deduced above. We can now obtain a corrected value for the ignition-point of electrolytic gas. This is given by

$$291{\cdot}7\left[\frac{377}{30{\cdot}2}\right]^{\gamma-1}$$

(see Dixon and Crofts, *loc. cit.*, p. 2043); putting $\gamma-1=0{\cdot}396$, we get the ignition-point as 520°.

Below is given the series of experiments on the ignition-points of mixtures of electrolytic gas and argon, the calculations being performed as shown in the case of the first mixture.

Mixtures of Electrolytic Gas with Argon.

TABLE I.

$2H_2+O_2+A.$

t_1.	V_2.	Result.	t_1.	V_2.	Result.
11·8	36·5	Explosion.	12·7	38·0	Explosion
11·9	37·5	Explosion	12·8	38·5	No explosion
12·1	38·5	No explosion	13·0	38·5	No explosion
12·5	37·8	Explosion	13·0	38·4	Explosion

The ignition-point is derived from $286\left[\frac{377}{38{\cdot}4}\right]$ (see below).

This temperature is roughly about 533°, and hence for electrolytic gas according to Lewis and Randall's formula $C_v=5{\cdot}01$ and $\gamma=1{\cdot}396$.

The temperature attained by the electrolytic gas if compressed alone is $286\left[\frac{377}{38{\cdot}4}\right]^{0{\cdot}396}=707$ abs., and the temperature attained by the argon, if considered alone, is $286\left[\frac{377}{38{\cdot}4}\right]^{0{\cdot}666}=1312$ abs.

Using the method of mixtures we have:

$$3\times 5{\cdot}01[T_\theta-707]=2{\cdot}981[1312-T_\theta],$$

from which $T_\theta=807$ abs. Therefore the ignition-point = 533°.

An alternative method of calculation which appears to be more applicable to the conditions, but is not so easy to follow, leads to the same result.

If the electrolytic gas of the mixture is supposed to be heated adiabatically to a temperature T_E a value of γ has to be used which is the mean between its value at the initial temperature T_1 and its value at T_E—this mass of gas at T_E is then supposed to be raised in temperature by mixture with a mass of argon at T_A; a new value of C_v for electrolytic gas now comes into play, namely, the mean value between the temperatures T_E and T_θ, the final temperature of the mixture.

The mixture is exploded at $V_2=38{\cdot}5$, when $T_1=286$; now the

electrolytic gas portion rises to a temperature of $286\left[\frac{377}{38{\cdot}5}\right]^{\gamma-1}$, which, using $\gamma=1{\cdot}4$, is roughly 712 abs. The value of γ between 286° and 712°, calculated as above, is 1·399; therefore,

$$T_E=286\left[\frac{377}{38{\cdot}5}\right]^{0{\cdot}39}=712.$$

Now the electrolytic gas at 712° is raised to T_θ by heat derived from the argon. The mean C_v between 712° and 808°, which we know is about the value of T_θ, is 5·21. T_A is obtained from $286\left[\frac{377}{38{\cdot}5}\right]^{0{\cdot}666}$ and comes to 1307 abs. Then by the method of mixtures,

$$3\times5{\cdot}21(\theta-712)=2{\cdot}981(1307-\theta),$$

whence $\theta=806$ abs. or 533°, as before.

Table II.

$2H_2+O_2+2A$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
14·0	45·7	No explosion	14·3	43·8	Explosion
14·0	43·7	Explosion	14·4	44·1	No explosion
14·1	44·7	No explosion	14·3	44·0	Explosion
14·2	44·3	No explosion			

Therefore, the ignition-point derived from $287{\cdot}3\left[\frac{377}{44{\cdot}0}\right]$, which, calculating as on page 297, = 547°.

Table III.

$2H_2+O_2+3A$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
13·8	48·0	Explosion	14·0	48·2	No explosion
13·8	49·0	No explosion	14·1	48·1	Explosion
13·9	48·5	No explosion			

Therefore, the ignition-point derived from $287{\cdot}1\left[\frac{377}{48{\cdot}1}\right]=554°$.

Table IV.

$2H_2+O_2+4A$

t_1.	V_2.	Result.	t_1.	V_2.	Result.
12·4	49·0	Explosion	13·4	49·8	Explosion
13·3	49·8	No explosion	13·5	50·5	No explosion
13·3	49·5	Explosion	13·5	50·0	No explosion

Therefore, the ignition-point derived from $286{\cdot}4\left[\frac{377}{49{\cdot}8}\right]=574°$.

TABLE V.

$2H_2+O_2+8A$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
12·8	50·0	No explosion	13·3	51·9	No explosion
12·8	42·8	Explosion	13·6	51·5	No explosion
12·9	47·8	Explosion	13·6	51·5	Explosion
13·0	49·9	Explosion	13·7	52·0	No explosion
13·3	50·9	Explosion	13·7	51·6	No explosion

Therefore, the ignition-point derived from $286{\cdot}6\left[\frac{377}{51{\cdot}5}\right]=630°$.

TABLE VI.

$2H_2+O_2+12A$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
13·7	50·7	No explosion	14·0	49·9	Explosion
13·7	44·7	Explosion	14·4	50·9	No explosion
13·8	47·9	Explosion	14·4	50·1	No explosion

Therefore, the ignition-point derived from $287\left[\frac{377}{50{\cdot}1}\right]=685°$.

These results may be summarised as follows:

Mixtures.	Ignition-point.
$2H_2+O_2$	520°
$2H_2+O_2+A$	533
$2H_2+O_2+2A$	547
$2H_2+O_2+3A$	554
$2H_2+O_2+4A$	574
$2H_2+O_2+8A$	630
$2H_2+O_2+12A$	685

The results, when plotted, give a graph which is nearly a straight line, the two last mixtures being somewhat too high. If the ignition-points are corrected by assuming that the curve is actually a straight line, the following ignition-points are obtained:

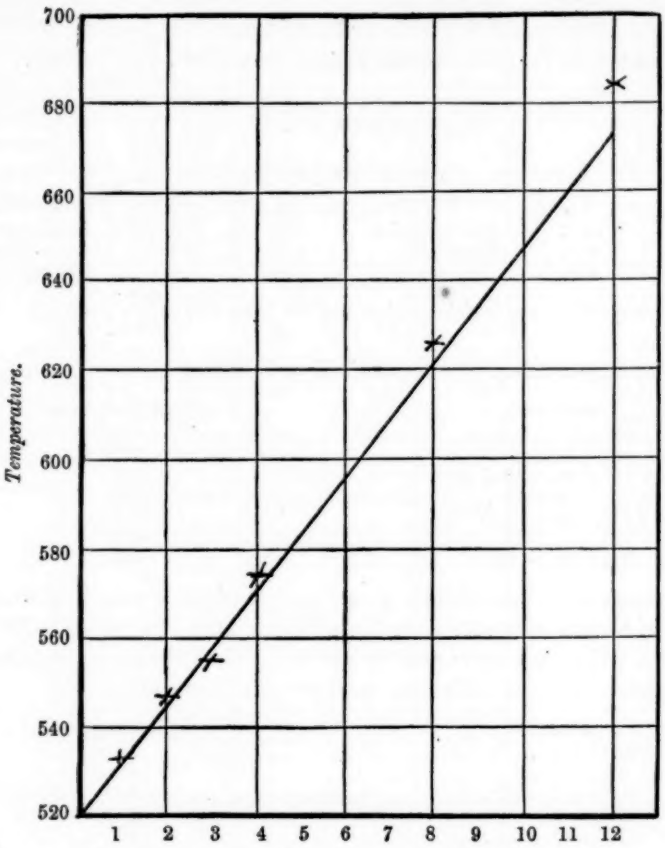
Mixtures.	Ignition-point.
$2H_2+O_2$	520°
$2H_2+O_2+A$	532
$2H_2+O_2+2A$	545
$2H_2+O_2+3A$	557
$2H_2+O_2+4A$	570
$2H_2+O_2+8A$	622
$2H_2+O_2+12A$	674

or, generally, the ignition-point of $2H_2+O_2+x$A is $520°+13x$.

Determination of Specific Heat of Nitrogen and Hydrogen.

The series of ignition-points, found above, of mixtures containing argon gives a basis to which the ignition-points of mixtures containing nitrogen and excess hydrogen may be referred. Dixon and Crofts have shown that mixtures of the type $2H_2+O_2+xN_2$ and

$2H_2 + O_2 + xH_2$ give curves for the ignition-points which are straight lines or practically straight lines when a value of 1·4 is taken for γ. It would seem, then, from this fact alone that the nitrogen or excess of hydrogen acts as the argon does in the mixtures, that is, as an inert gas. This one would expect from theoretical considerations to be the case, at any rate with nitrogen. It may therefore



be concluded that the actual ignition-points of these mixtures containing nitrogen or excess of hydrogen are close to those which have been found above for the corresponding argon mixture.

As an instance, Dixon and Crofts (*loc. cit.*, p. 2049) find the ignition-point of the mixture $2H_2 + O_2 + N_2$ to be 537° when γ is taken as 1·4 for all the individual gases in the mixture; but the argon mixture $2H_2 + O_2 + A$, which corresponds with the nitrogen

mixture, gives an ignition-point of 532°; this, *ex hypothesi*, should be the actual ignition-point of the nitrogen mixture also. Hence, taking for the electrolytic-gas portion of the mixture the value of γ and C_v found previously, a value for nitrogen (or hydrogen) can be obtained by a calculation (similar to that already used), which is set out in full in the case of the first mixture given below.

Nitrogen Mixtures.

The mixture, $2H_2+O_2+N_2$, explodes at $V_2=29{\cdot}7$ ($V_1=377$ as always) when $T_1=293{\cdot}1$ (see Dixon and Crofts for the data for the nitrogen and hydrogen mixtures). This gives an ignition-point calculated from the corresponding argon mixture of 532° or 805 abs. Now up to this temperature electrolytic gas has $C_v=5{\cdot}01$ and $\gamma=1{\cdot}396$ (see page 297). We have then for the latter part of the mixture a temperature on compression corresponding with $293{\cdot}1\left[\frac{377}{29{\cdot}7}\right]^{0{\cdot}396}=801$ abs. This must, therefore, receive heat from the nitrogen in order that the final temperature may be 805 abs.; this amount of heat for three volumes of electrolytic gas is $3\times5{\cdot}01(805-801)=60{\cdot}1$ calories. This heat is given up by the nitrogen cooling through $y°$, so that if x is the molecular heat (C_v) of nitrogen, $xy=60{\cdot}1$. Now x roughly $=5$, therefore $y=12°$ about, so that the nitrogen was cooled from 817 to 805 abs.; therefore $293{\cdot}1\left[\frac{377}{29{\cdot}7}\right]^{\gamma-1}$ must in the case of nitrogen give 817 abs. or thereabouts. The full equation for the mixtures may now be stated:

$$3\times5{\cdot}01(805-801)=x\left[293{\cdot}1\left(\frac{377}{29{\cdot}7}\right)^{\frac{1{\cdot}98}{x}}-805\right],$$

whence $x=4{\cdot}913$ and $\frac{1{\cdot}985}{x}=1{\cdot}404$.

That is, $\gamma=1{\cdot}404$ and $C_v=4{\cdot}913$ as mean values between the temperatures concerned.

The mixture, $2H_2+O_2+2N_2$, explodes at $V_2=27{\cdot}0$ when $T_1=286{\cdot}3$. The corresponding argon mixture has an ignition-point of 545° or 818 abs.; when, making the necessary alteration for the effect of increased temperature on the value of C_v and γ for electrolytic gas, we have:

$$3\times5{\cdot}018(818-812)=2\times x\left[286{\cdot}3\left(\frac{377}{27{\cdot}0}\right)^{\frac{1{\cdot}985}{x}}-818\right],$$

whence $\gamma=1{\cdot}403$ and $C_v=4{\cdot}926$.

The mixture $2H_2+O_2+4N_2$ explodes at $V_2=25{\cdot}7$ when $T_1=288{\cdot}4$. The corresponding argon mixture has an ignition-point of 570° or 843 abs.

Then as before:

$$3 \times 5{\cdot}03(843-833)=4x\left[288{\cdot}4\left(\frac{377}{25{\cdot}7}\right)^{\frac{1{\cdot}985}{x}}-843\right],$$

whence $\gamma=1{\cdot}403$ and $C_v=4{\cdot}926$.

The mixture $2H_2+O_2+8N_2$ explodes at $V_2=22{\cdot}5$ when $T_1=287{\cdot}5$. The corresponding argon mixture has an ignition-point of 622° or 895 abs.

Then as before:

$$3 \times 5{\cdot}048(895-871)=8x\left[287{\cdot}5\left(\frac{377}{22{\cdot}5}\right)^{\frac{1{\cdot}985}{x}}-895\right],$$

whence $\gamma=1{\cdot}406$ and $C_v=4{\cdot}889$.

The mixture $2H_2+O_2+14N_2$ explodes at $V_2=17{\cdot}4$ when $T_1=287{\cdot}6$. The corresponding argon mixture has an ignition-point of 702° or 975 abs.

Then as before:

$$3 \times 5{\cdot}08(975-962)=14x\left[287{\cdot}6\left(\frac{377}{17{\cdot}4}\right)^{\frac{1{\cdot}985}{x}}-977\right],$$

whence $\gamma=1{\cdot}398$ and $C_v=4{\cdot}988$.

To summarise these results for nitrogen we have, taking $t_1=15°$ ($T_1=288$):

Temperature interval.	Mean value of γ.	Mean value of C_v.
15°–532°	1·404	4·913
15 –545	1·403	4·926
15 –570	1·403	4·926
15 –622	1·406	4·889
15 –702	1·398	4·988

Mixtures containing Excess of Hydrogen.

The mixture, $2H_2+O_2+H_2$, explodes at $V_2=27{\cdot}6$ when $T_1=287{\cdot}2$. The corresponding argon mixture has an ignition-point of 532° or 805 abs.

Then, calculating as shown fully under the nitrogen mixtures, $\gamma=1{\cdot}389$, $C_v=5{\cdot}103$.

The mixture, $2H_2+O_2+2H_2$, explodes at $V_2=26{\cdot}1$ when $T_1=286{\cdot}6$. The corresponding argon mixture has an ignition-point of 545° or 818 abs., whence $\gamma=1{\cdot}389$, $C_v=5{\cdot}103$.

The mixture, $2H_2+O_2+4H_2$, explodes at $V_2=23{\cdot}4$ when $T_1=288{\cdot}1$. The corresponding argon mixture has an ignition-point of 570° or 843 abs., whence $\gamma=1{\cdot}380$, $C_v=5{\cdot}223$.

The mixture, $2H_2+O_2+8H_2$, explodes at $V_2=19{\cdot}0$ when $T_1=286{\cdot}4$ (in the paper by Dixon and Crofts, by a misprint T_1 is given as $=287{\cdot}4$). The corresponding argon mixture has an ignition-point of 622° or 895 abs., whence $\gamma=1{\cdot}377$, $C_v=5{\cdot}268$.

The mixture, $2H_2+O_2+13H_2$, explodes at $V_2=15{\cdot}3$ when $T_1=287{\cdot}4$. The corresponding argon mixture has an ignition-point of 689° or 962 abs., whence $\gamma=1{\cdot}374$, $C_v=5{\cdot}311$.

To summarise these results for hydrogen, taking $t_1=15°$ ($T_1=288$):

Temperature interval.	Mean value of γ.	Mean value of C_v.
15°–532°	1·389	5·103
15 –545	1·389	5·103
15 –570	1·380	5·223
15 –622	1·377	5·268
15 –689	1·374	5·311

Discussion of Results.

Nitrogen.—As the difference C_p-C_v has been taken constant at 1·985 it matters little whether the values for γ or those for C_v are compared with the values of other experimenters; but since more work has been done on C_v it will be advisable to deal mainly with this. The figures found show an increase with temperature, the actual increase in C_p being 0·0075 over a range of 170°, and an average value of 4·945 between 15° and 590° roughly. Below, this figure is compared with those calculated from the values of other observers for the mean C_v between 15° and 590°:

Mean Value of C_v *for Nitrogen.*

Mallard and Le Chatelier	5·4798
Le Chatelier	4·8453
Langen	5·1840
Pier	5·1655
Holborn and Henning (from C_p)	4·7003
Stevens (from γ, for air)	about 5·2980
Kalähne „ „	„ 5·0260
Fürstenau „ „	„ 4·9710
Lewis and Randall (general review)	5·0750
Crofts	4·9450

To this last may be added the value 4·918 calculated for a pressure of 18 atmospheres, but at the ordinary temperature, by the use of the formula given by Holborn and Jakob (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 213).

The first four values were obtained by means of the explosion method in which changes of pressure as well as changes of temperature take place, the maximum temperature, however, being considerably higher than those obtaining in the present experiments; the next four values were obtained at pressures at or near atmospheric. The figures quoted show considerable variation, from a minimum of 4·7003 (Holborn and Henning) to a maximum of 5·4798 (Mallard and Le Chatelier) with a mean of 5·083; the value found, namely, 4·928, is within 3·2 per cent. of this mean value. One would perhaps expect the value of γ found by this method to be high, and hence the C_v as calculated here too low owing to the high pressures under which the experiments are performed, varying from a mean of 18 atmospheres in the mixture

$2H_2+O_2+N_2$ to a mean of 36 atmospheres in the mixture $2H_2+O_2+14N_2$. On the other hand, the loss of heat by conduction from the compressed gas would tend to make γ small and C_v large.

The values found for the mean value of C_v for nitrogen may be expressed by the formula $C_v=4{\cdot}7+0{\cdot}0004t$ as under, the calculated and observed values being placed side by side for comparison.

Temperature interval.	C_v calc.	C_v observed.	Difference. Per cent.
15°–532°	4·913	4·913	0
15 –543	4·917	4·926	−0·18
15 –570	4·928	4·926	+0·04
15 –622	4·949	4·889	+1·2
15 –702	4·981	4·988	−0·14

The agreement is good except in the last value but one, where it is evident that the explosion point found for the nitrogen mixture must have been at fault.

Hydrogen.—For hydrogen there are not very many figures with which to compare the values of C_v. Many observers (Mallard and Le Chatelier, Langen and others) include hydrogen with other diatomic gases, and give figures which are identical with those given for nitrogen. The mean value of the figures given on page 303 is $C_v=5{\cdot}208$ at 590°. With this we can compare 4·9655 found by means of Pier's formula and 5·018 by the use of Lewis and Randall's formula. Experiments on the value of γ at high temperatures and pressures are few; at ordinary temperatures, however, adiabatic methods give a small value for γ and a correspondingly large one for C_v. Röntgen (*Ann. Phys. Chem.*, 1873, [ii], **148**, 580) has γ, which gives $C_v=5{\cdot}153$, Manœuvrier (*Ann. Chim. Phys.*, 1895, [vii], **6**, 321) 5·170, whilst Lummer and Pringsheim (*Ann. Phys. Chem.*, 1898, [iii], **64**, 553), whose work carries weight, give 4·862, a much lower value than the others just quoted. Lussana (*loc. cit.*) finds C_p (not C_v)$=6{\cdot}804$ at one atmosphere pressure and 7·576 at 30 atmospheres pressure.

The values obtained, therefore, are well within the limits found by other experimenters; they may be somewhat high owing to the high conductivity of the gas and consequent loss of heat during compression. The figures may be expressed by the equation:

$$C_v=4{\cdot}860+0{\cdot}00064t.$$
(15 . t)

Temperature interval.	C_v calc.	C_v observed.	Difference. Per cent.
15°–532°	5·200	5·103	+1·9
15 –543	5·207	5·103	+2·0
15 –570	5·224	5·223	+0·02
15 –622	5·264	5·268	−0·07
15 –689	5·301	5·311	−0·19

The agreement with the last three values is good, but that with the first two is far from satisfactory, and it is evident that a formula containing higher powers of t would better meet the case; as the number of values found is not large, it was not thought desirable to endeavour to obtain exact agreement; the formula $C_v = 4{\cdot}7 + 0{\cdot}001t - 0{\cdot}0000002t^2$ expresses the last three values with (15.1) much exactness, and gives for the five given intervals of temperature the value 5·194, 5·202, 5·223, 5·263, and 5·312 respectively for C_v.

From the experiments described above a value for electrolytic gas and a value for hydrogen have been found; it is possible, therefore, to deduce from these a value for oxygen; such a value is subject to the errors in the two determinations from which it is derived, and is therefore not inserted here. A direct value for oxygen cannot be obtained by experiments similar to those already given, since it has been pointed out by Dixon and Crofts that the addition of oxygen to electrolytic gas lowers the ignition-point progressively, and no satisfactory explanation of this point has yet been offered.

Note.—The considerable quantities of argon required in these experiments were prepared by a method due to Fischer and Runge (*Ber.*, 1908, **41**, 2017). Air was passed into a steel cylinder containing a mixture of calcium carbide and calcium chloride heated by means of an electric furnace. The crude argon so obtained contains impurities such as carbon monoxide, hydrocarbons, etc., and these were removed by passing the gas over heated copper oxide and absorbing the carbon dioxide and water formed. The argon was purified by circulating it over heated metallic calcium, and the purity tested by finding the vapour density. Argon of moderate purity can be obtained by the action of the calcium carbide mixture alone without the use of metallic calcium, but where large amounts of the gas are required time is saved by pumping off the crude argon from the steel cylinder, and passing it over the calcium without waiting until absorption of nitrogen and oxygen is complete, as this action becomes slower and slower as the carbide becomes used up.

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[*Received, Jan. 29th*, 1915.]

XXXV.—*The Firing of Gases by Adiabatic Compression. Part IV. The Ignition-Points of Mixtures of Electrolytic Gas with Carbon Dioxide. Ratio of the Specific Heats for Carbon Dioxide.*

By James Murray Crofts.

As the addition of a monatomic gas to the diatomic constituents of electrolytic gas gave such interesting results under adiabatic compression, it was thought advisable to investigate the conditions for ignition of a series of mixtures containing a triatomic gas. Carbon dioxide appeared to be the most suitable gas for this purpose, and mixtures of the general formula $2H_2+O_2+xCO_2$ were prepared, and the conditions for explosion under adiabatic compression were investigated. It was not possible to determine the conditions of explosion of electrolytic gas diluted with carbon dioxide to the same extent as with nitrogen, argon, etc., owing to the fact that the ratio of the specific heats for this triatomic gas is small, and therefore considerable compression is required in order to fire the gas when very much diluted; the final volume of the mixture in such cases is small, and the error in obtaining its value relatively large.

A discussion of the figures given by various experimenters for the value of γ for carbon dioxide is given after the experimental part of this paper; it is necessary to state here that such figures lead, when applied to the experimental data, to a series of ignition-points which do not agree with those obtained from the argon series (see preceding paper). Taking the formula given by Lewis and Randall for the specific heat at constant pressure, namely,

$$C_p=7{\cdot}0+0{\cdot}0071T-0{\cdot}00000186T^2,$$

we can, as shown in the previous paper, using the method of mixtures, obtain a value for the ignition-point. For instance, from table I below it is seen that the mixture $2H_2+O_2+CO_2$ explodes at $V_2=20{\cdot}8$ when $T_1=288{\cdot}7$. This should give an ignition-point of 532°, corresponding with that given by the corresponding argon mixture, $2H_2+O_2+A$. Calculating from the above formula, $C_v=8{\cdot}21$ and $\gamma=1{\cdot}241$. Using these figures and calculating in the usual manner, we get the final temperature of the mixture = 793 abs. or 520°. Thus it would appear that the addition of carbon dioxide to the extent of 33 per cent. of the electrolytic gas taken has no effect on the ignition-point of the mixture. Judging by the effects of the addition of other gases, this is not probable, and evidently the value of γ used is too small. The experimental data, then, were

used as in Part III, dealing with nitrogen and hydrogen, to obtain values for γ and the molecular heat at constant volume for carbon dioxide.

Before proceeding to deal with the explosion data it was thought desirable to see whether any chemical action took place between the gases in the mixture beyond the combination of hydrogen and oxygen to form water. Berthelot (*Ann. Chim. Phys.*, 1898, [vii], **14**, 167), although he gives no experimental details, states that if a mixture of oxygen, hydrogen, and carbon dioxide, the two former in the proportion to form water, is ignited and exploded, the hydrogen is completely burnt to water without any action on the carbon dioxide taking place. If the hydrogen is by itself or has insufficient oxygen with it to produce complete oxidation, then some of the carbon dioxide is reduced to carbon monoxide. This fact is well known, but in support the work of Dixon (T., 1886, **49**, 94) and of Boudouard (*Bull. Soc. chim.*, 1901, [iii], **25**, 485) may be quoted. It was thought well, however, to investigate the case under the actual conditions of the adiabatic compression.

Hydrogen and carbon dioxide were mixed in different proportions, and the mixed gas compressed to temperatures roughly corresponding with the ignition-points of the $2H_2+O_2+xCO_2$ mixtures, in which the hydrogen and carbon dioxide were in the same relative proportion to one another. After compression the gases were withdrawn from the explosion chamber and analysed in a Bone and Wheeler gas analysis apparatus. The details are as follows:

(1) The mixture $2H_2+CO_2$ was compressed to $V_2=18{\cdot}0$, T_1 being $287{\cdot}9$; thus $T_2=540°$ roughly. On analysis the percentage composition was:

	Before compression.
$CO_2=33{\cdot}02$	$CO_2=33{\cdot}04$
$H_2=66{\cdot}9$	$H_2=66{\cdot}96$
$CO=0{\cdot}08$	—

(2) H_2+CO_2 compressed to $V_2=13{\cdot}4$, T_1 being $287{\cdot}3$; thus T_2 was roughly 557° (see table III below). Analysis:

After compression.	Before compression.
$CO_2=47{\cdot}51$	47·55
$H_2=52{\cdot}43$	52·45
$CO=0{\cdot}06$	—

(3) $2H_2+5CO_2$ compressed to $V_2=5{\cdot}0$, T_1 being $286{\cdot}9$, T_2 working out at about 720°, the value of γ for carbon dioxide being doubtful at this temperature. Analysis:

After compression.	Before compression.
$CO_2=68{\cdot}9$	69·1
$H_2=31{\cdot}0$	30·9
$CO=0{\cdot}1$	—

In these analyses the average amount of carbon monoxide found was only 0·08 per cent., a figure exceedingly small; so small, in fact, as to be scarcely outside the error of observation in conducting the analyses.

These analyses might usefully be compared with one of a mixture, $2H_2 + O_2$, compressed to a temperature just under the ignition-point (520°):

After compression.	Before compression.
H_2 = 66·68	66·70
O_2 = 33·26	33·29
CO = 0·06	=

Here, again, a minute quantity of carbon monoxide appears to be present; but in this case it can come only from a partial burning of the lubricant, or charring of the leather washer fitted to the piston. One may conclude, therefore, that at the temperatures under consideration the amount of reduction of the carbon dioxide effected by the hydrogen, if any, is extremely small, and is not sufficient to affect the action of a mixture, $2H_2 + O_2 + xCO_2$, in the cylinder.

After any explosion, however, carbon monoxide is always found in the cylinder, along with carbon dioxide. This, as already explained (Dixon and Crofts, *loc. cit.*, p. 2040), is an after-effect of the explosion, and is produced from the lanoline as the piston is being pushed back. The subjoined analyses taken after the explosion of a mixture, $2H_2 + O_2 + 3CO_2$, throw light on this point, and confirm the statement made above that in the mixture the hydrogen and oxygen burn completely to water. Four different experiments were performed. In (*a*) a large amount of lanoline was used; the amounts were reduced in (*b*) and (*c*), and in (*d*) none at all was put on the leather, which, of course, had been used for some time, and was well impregnated with lubricant. The figures given are calculated on the original amount of gas, the final volume being reckoned as 50 per cent. of the original, and the initial composition is given under (*e*) for purposes of comparison. After removal of carbon monoxide some gas remained, which exploded when mixed with oxygen and sparked. This is termed "hydrocarbon" in the analyses, and proceeds from the lanoline:

	(*a*.)	(*b*.)	(*c*.)	(*d*.)	(*e*.)
CO_2	43·9	45·3	46·7	47·3	49·3
CO	2·3	1·3	0·9	0·5	—
Hydrocarbon and Residual N_2	3·8	3·4	2·4	2·2	—
	—	—	—	—	1·2

These figures, as they stand, need correction; they show fairly correctly the amounts of monoxide formed, but they make it appear

that large amounts of dioxide are attacked. This, however, is not the case, as additional gas is formed by the explosion, as shown as follows: The original volume of gas, $V_1=37{\cdot}7$, and the pressure of this gas was noted by the manometer; after explosion the volume of gas left by this particular mixture (50 per cent. of carbon dioxide) should be $\frac{37{\cdot}7}{2}=18{\cdot}85$ at the same pressure; actually, however, three successive experiments under conditions (*d*) gave this amount as 19·4, 19·4, and 19·5; taking the value 19·4 as correct, we have by the analysis that 94·6 per cent. ($2\times47{\cdot}3$) of this is carbon dioxide, $\frac{94{\cdot}6}{100}\times19{\cdot}4=18{\cdot}55$, and this in turn is 49·2 per cent. of 37·7, the original volume of gas taken. This figure, 49·2 per cent. compared with 49·3 per cent.—the figure given for the original gas under (*e*) above—shows that little, if any, reduction of the dioxide has taken place.

Subjoined are the records of experiments conducted to find the ignition-points of mixtures $2H_2+O_2+xCO_2$ (*N* denotes a non-explosion and *X* an explosion):

TABLE I.

$2H_2+O_2+CO_2$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
15·5	18·8	*X*	15·4	20·3	*X*
15·6	21·8	*N*	15·6	20·8	*N*
15·7	19·8	*X*	15·6	20·5	*X*
15·8	20·8	*N*	15·7	20·7	*X*
15·9	20·3	*X*			

Ignition-point is derived from $288{\cdot}7\left[\frac{377}{20{\cdot}7}\right]$ (see below).

TABLE II.

$2H_2+O_2+2CO_2$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
15·0	16·5	*N*	15·4	16·3	*N*
15·1	16·0	*X*	15·4	16·1	*X*
15·1	16·3	*N*	15·5	16·2	*X*
15·2	16·1	*X*			

Ignition-point is derived from $288{\cdot}5\left[\frac{377}{16{\cdot}2}\right]$.

TABLE III.

$2H_2+O_2+3CO_2$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
15·2	11·8	*X*	15·6	13·5	*N*
15·3	12·8	*X*	15·7	13·4	*X*
15·4	13·8	*N*	15·8	13·6	*N*
15·5	13·3	*X*			

Ignition-point is derived from $288{\cdot}7\left[\frac{377}{13{\cdot}4}\right]$.

TABLE IV.

$2H_2+O_2+4CO_2$.

t_1.	V_2.	Result.	t_1.	V_2.	Result.
15·3	9·9	*X*	15·5	11·0	*X*
15·3	10·1	*X*	15·5	11·6	*N*
15·4	11·0	*X*	15·6	11·3	*X*
15·5	12·0	*N*	15·6	11·4	*N*

Ignition-point is derived from $288{\cdot}6\left[\frac{377}{11{\cdot}3}\right]$.

These experimental data were now used to obtain values for the ratio of the specific heats; the mode of calculation is similar to that set out in the previous paper on the specific heats of nitrogen and hydrogen, and need not be detailed again.

The assumption is made that mixtures of electrolytic gas with carbon dioxide have the same ignition-point as corresponding mixtures with argon. This assumption, although perhaps not absolutely correct, does not appear to be wide of the mark.

(1) Mixture $2H_2+O_2+CO_2$ explodes at $V_2=20{\cdot}7$ when $T_1=288{\cdot}7$. The corresponding argon mixture has an ignition-point of $532°=805$ abs.

From this, for CO_2, $\gamma=1{\cdot}254$ and $C_v=7{\cdot}815$.

(2) Mixture $2H_2+O_2+2CO_2$ explodes at $V_2=16{\cdot}2$ when $T_1=288{\cdot}5$. The corresponding argon mixture has an ignition-point of 545° or 818 abs.

From this, for CO_2, $\gamma=1{\cdot}253$ and $C_v=7{\cdot}847$.

(3) Mixture $2H_2+O_2+3CO_2$ explodes at $V_2=13{\cdot}4$ when $T_1=288{\cdot}8$. The corresponding argon mixture has an ignition-point of 557° or 830 abs.

From this, for CO_2, $\gamma=1{\cdot}252$ and $C_v=7{\cdot}878$.

(4) Mixture $2H_2+O_2+4CO_2$ explodes at $V_2=11{\cdot}3$ when $T_1=288{\cdot}6$. The corresponding argon mixture has an ignition-point of 570° or 843 abs.

From this, for CO_2, $\gamma=1{\cdot}251$ and $C_v=7{\cdot}909$.
Tabulating these results, and using t_1 as 15 approximately:

Temperature-interval.	Mean value of γ.	Mean value of C_v.
15°–532°	1·254	7·815
15 –545	1·253	7·847
15 –557	1·252	7·878
15 –570	1·251	7·909

These figures cannot well be compared with those of other observers owing to the fact that rapid changes of temperature and pressure are going on at the same time. Many experiments have been conducted on carbon dioxide at ordinary temperatures and pressures; perhaps the most trustworthy are those of Lummer and Pringsheim (*Ann. Phys. Chem.*, 1898, [iii], **64**, 553), who give for γ the value 1·2995. Makower (*Phil. Mag.*, 1903, [vi], **5**, 226) gives $\gamma=1{\cdot}307$. Moody (*Physikal. Zeitsch.*, 1912, **13**, 383) finds $\gamma=1{\cdot}3003$. Evidently the figure is very close to 1·30.

For the specific heat at constant volume, under ordinary conditions of temperature and pressure there are few direct determinations. Joly (*Proc. Roy. Soc.*, 1894, **55**, 390) gives an equation for the specific heat, from which the molecular heat C_v works out at 7·3 (at a pressure of one atmosphere). This is higher than the figure derived from the value for C_p found by other observers, as is also evident from the fact that if in the equation $C_v=\dfrac{1{\cdot}985}{\gamma-1}$ we substitute 1·3 for γ, then $C_v=6{\cdot}62$.

The effect of rise of temperature alone has been studied by many observers. In all cases a decrease in the value of γ with rise of temperature has been found, and presumably an increase in the value of C_v (for references see above). In addition, Fürstenau (*Ann. Physik*, 1908, [iv], **27**, 735), by measuring the wave-lengths of sound, found $\gamma=1{\cdot}2506$ at 484·5° and 1·3008 at room temperature; taking the mean temperature of the compressed mixture $2H_2+O_2+CO_2$ as 273°, Fürstenau's experiments would give an approximate value 1·284.

The effects of pressure have not received so much careful study. Joly (*loc. cit.*) finds an increase in C_v up to a certain density, beyond which there is a decrease; the value of γ varies inversely with this. Under a pressure of 26 atmospheres, which is roughly the mean obtained in compressing the mixture $2H_2+O_2+CO_2$, Joly's equation gives $C_v=7{\cdot}4$. Amagat (*Compt. rend.*, 1895, **121**, 802), by the pressure method, finds an increase in the value of γ, as also does Thibaut (*Ann. Physik*, 1911, [iv], **35**, 373).

Worthing (*Phys. Rev.*, 1911, **33**, 217) investigated the changes

in value of γ under varying conditions of temperature and pressure; for example:

At $P=$ 7·78 atmos.	$=1·338$ at	0·2°
	$=1·310$ „	31
	$=1·296$ „	50
	$=1·256$ „	98·5
At $P=28·52$ atmos.	$=1·702$ „	0·2
	$=1·499$ „	31
	$=1·448$ „	50
	$=1·327$ „	98·5

It is evident, therefore, that the effects of temperature and pressure work against one another in the case of the ratio γ.

For the combined effects of rise of temperature and pressure on the value of C_v, the explosion method of Mallard and Le Chatelier (*Ann. des Mines*, 1884, **4**, 378) is in its conditions somewhat comparable to the present method. These observers ignite, by means of a spark, an explosive mixture of gases, and observe the pressure generated by the explosion; knowing the amount of heat generated by the chemical action, one can, by means of the gas equation $PV=RT$, easily calculate the specific heats. In such experiments both temperature and pressure rise suddenly to high values, the maximum temperature being much higher than the ignition-points found in the present series of experiments. Mallard and Le Chatelier give a linear formula $6·5+0·00387t$ for mean C_v in the case of carbon dioxide; and later, Le Chatelier (*Compt. rend.*, 1887, **104**, 1780) gives $C_v=6·5+0·0037T$. Langen (*Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesen*, 1903, 8), who improved on the method, gives mean $C_v=6·7+0·0026t$. More recently Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536; 1910, **16**, 897), still further improving on the method of estimating the pressure produced by the explosion, gives:

$$C_v=6·8+3·3\times10^{-3}t-0·95\times10^{-6}t^2+0·1\times10^{-9}t^3.$$

This equation gives results which agree very fairly with those deduced from the value of C_p (by using the relation $C_p-C_v=1·985$) found by Holborn and Henning (*Ann. Physik*, 1907, [iv], **23**, 809) by the Regnault method.

In Part III. (p. 293) reference was made to work conducted by Clerk and by Hopkinson on the adiabatic compression of air and of carbon dioxide. The latter states (*Brit. Assoc. Reports*, 1910, 199) that the values obtained by him for C_v in the case of carbon dioxide are close to those deduced from Swann's results for C_p by extrapolation. Swann's results, both for air and for carbon dioxide, are higher than those of other observers who have employed the same method; for example, for carbon dioxide between 0° and 550° Swann's figures would give $C_v=9·5$, which

value can be compared with those tabulated below. It should be mentioned again that Hopkinson assumed that the value of γ remained constant during the course of his experiments.

Finally, Lewis and Randall, as already stated, in considering all these figures, drew the conclusion that $C_p = 7{\cdot}0 + 0{\cdot}0071T - 0{\cdot}00000186T^2$, from which, in view of the data employed, we may deduce $C_v = 5{\cdot}0 + 0{\cdot}0071T - 0{\cdot}00000186T^2$.

The figures given by various observers for the mean value of C_v between 0° and 550° (the average final temperature of the mixtures given in this paper) are given below:

Mallard and Le Chatelier	8·628
Le Chatelier	8·527
Langen	8·13
Pier	8·344
Holborn and Henning	8·415
Fürstenau (about)	7·0
Joly	7·4
Lewis and Randall	8·191
Crofts	7·862

The first four figures are obtained from explosion methods; they are comparatively high, but not higher than that obtained by Holborn and Henning using Regnault's stream method to find C_p. Adiabatic methods give low figures, although not low in comparison with Joly's direct observation of C_v. Where there is such considerable variation in the values found by different experimenters and in the different conditions under which the various experiments were performed, it is of little value to push comparisons very far. At least it can be said that the values obtained by the present method are consistent and probable.

The four values found can be well expressed by means of the linear formula $C_v = 6{\cdot}6 + 0{\cdot}0023t$ (15 . t); they do not, however, cover a large range of temperature, the maximum being 532° in the first case and 570° in the last.

Temperature-interval.	C_v calculated.	C_v observed.	Difference. Per cent.
15°–532°	7·823	7·815	−0·1
15 –545	7·853	7·847	−0·08
15 –557	7·881	7·878	−0·04
15 –570	7·911	7·909	−0·03

I wish to express my thanks to Professor H. B. Dixon, in whose laboratory the work described in this and in the preceding paper has been performed.

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[*Received, Jan. 29th*, 1915.]

XXXVI.—*Volatile Oil from Tubers of* Kaempferia ethelæ.

By Ernest Goulding and Oswald Digby Roberts.

A small sample of the tubers of *Kaempferia Ethelae*, J. M. Wood, was forwarded to the Imperial Institute from the Transvaal in 1909 by the Director of Agriculture, who stated that these so-called "Sherungulu" tubers are dried and sent up from the low country for sale to the workers on the Rand, by whom they are supposed to have medicinal or other virtues. The plant grows in large quantities in the extreme north-east of the Transvaal, and could easily be cultivated.

An examination of the sample, which consisted of tubers and rootlets, showed that it contained 42·2 per cent. of water. When distilled in a current of steam it yielded a pale yellow, mobile oil, having a rather pleasant odour, somewhat resembling that of orange-flower oil, combined with a less agreeable smell, recalling that of crushed ivy leaves. The quantity of oil obtained amounted to 1·1 per cent. of the material as received, or 1·9 per cent. expressed on the weight of the dried material. It had D^{15}_{15} 0·936 and $[\alpha]_D$ +30·4°.

A larger quantity of the tubers was received in 1911, and when 31·8 kilos. of the material were distilled in a current of steam there were obtained 440 grams of a light oil and 33 grams of a heavy oil, equivalent to a total yield of 1·5 per cent. As the tubers contained 25 per cent. of moisture, the yield on the dried material amounted to 2·0 per cent.

Examination of the Light Oil.

This portion, which constituted 93 per cent. of the total distillate, was pale yellowish-brown, had the same odour as the preliminary specimen of oil already described, and furnished the following constants:

D^{15}_{15}	0·9437
α^{22}_{D} in 100 mm. tube.....	+19°47′
Acid value	2·3
Ester value	5·0

(Corresponding with 1·75 per cent. of esters, calculated as $C_{10}H_{17}OAc$, or 1·4 per cent. calculated as $NHMe{\cdot}C_6H_4{\cdot}CO_2Me$).

Ester value after acetylation ..... 47·6

(Corresponding with 12·1 per cent. of free alcohols calculated as $C_{10}H_{17}{\cdot}OH$ and 1·75 per cent. of esters, calculated as $C_{10}H_{17}OAc$ or 1·4 per cent. calculated as $NHMe{\cdot}C_6H_4{\cdot}CO_2Me$).

Fractional Distillation of the Oil.

On distilling the oil under 20 mm. pressure in an atmosphere of carbon dioxide the following fractions were obtained:

		Boiling Point.			
		under 20 mm.	under atmospheric		α_D in 100 mm.
Fraction.	Per cent.	pressure.	pressure.	D_{15}^{15}	tube.
I.	42	70—80°	160—195°	0·9010	−4°30′
II.	25	80—135°	195—270°	0·9880	+26°30′

The residue, amounting to 33 per cent. of the oil, deposited colourless crystals in quantity equivalent to about 8 per cent. of the original oil. When this crystalline substance had been removed by filtration, the filtered oil had D_{15}^{15} 0·9967, but was too dark in colour to admit of the determination of its optical activity.

Terpenes: Identification of Dipentene.

The odour and other characters of fraction I indicated that it consisted chiefly of terpenes and cineole. After the removal of cineole by shaking the fraction with 50 per cent. solution of resorcinol, the oil was repeatedly distilled over sodium in a vacuum, and was finally obtained as a colourless, mobile liquid, which had D_{15}^{15} 0·8469, α_D^{22} in 100 mm. tube −5°25′, and boiled at 158—183° under atmospheric pressure. On distillation, about 30 per cent. boiled at 158—162°, 20 per cent. between 162° and 175°, 40 per cent. at 175—179°, and 10 per cent. at 179—183°. The fraction boiling at 158—162° had D_{15}^{15} 0·856 and α_D^{22} −4°25′, and probably consisted largely of pinene, which boils at 155—156°, and has D_{15} 0·863. The fraction boiling at 175—179° had D_{15}^{15} 0·845 and α_D^{22} −1°10′, and contained dipentene, which was identified by means of its tetrabromide melting at 124°. (Dipentene boils at 175—176°, and has D^{20} 0·844; its tetrabromide melts at 124—125°.)

Identification and Estimation of Cineole.

As already stated, the odour of fraction I indicated the presence of cineole. This was confirmed by the preparation of the iodole additive compound, which was obtained in yellowish-green crystals melting at 112°.

An estimation of cineole by the resorcinol method showed that fraction I contained 44 per cent. of this substance, equivalent to 18·5 per cent. in the original oil.

Acids and Phenols.

The free acids in the oil were extracted by shaking it with dilute sodium carbonate. On acidifying the solution and extracting with

ether, a small quantity of acids was obtained amounting to about 0·2 per cent. of the original oil, and possessing the odour of acetic acid.

After the removal of the acids the oil was shaken with 5 per cent. solution of sodium hydroxide. The solution was acidified with dilute sulphuric acid, and extracted with ether. On evaporation, the ethereal solution yielded a residue, consisting of a brown, viscous liquid with a creosote-like odour, and amounting to 0·6 per cent. of the original oil; owing to the small quantity available, this product was not further investigated.

Alcohols: Identification of Linalool.

As the odour of the oil suggested the presence of linalool a fraction boiling at 190—205° was oxidised with chromic acid mixture. The oily layer was separated, placed in a flask with dilute sodium carbonate, and distilled in a current of steam. The distilled oil was treated with sodium hydrogen sulphite solution, from which citral was subsequently liberated by the addition of sodium hydroxide. This substance was readily recognised by its characteristic odour, and was identified by the preparation of citrylidenecyanoacetic acid, which, after recrystallisation, melted at 120—121°. The presence of linalool in the oil was thus confirmed.

Examination of Esters: Identification of Methylanthranilic Acid.

A portion of the oil, after being freed from acids and phenols by treatment with sodium hydroxide solution, was boiled with alcoholic potassium hydroxide in order to hydrolyse the esters, and the resulting solution was shaken with a large excess of solution of sodium chloride. A solid substance separated, which was found to be a product of the action of the alcoholic potassium hydroxide on the crystalline constituent of the oil described in the following section. The aqueous-alcoholic liquid was heated on the water-bath to expel the alcohol, and then extracted repeatedly with ether. Dilute sulphuric acid was added to the concentrated solution in order to liberate the acids, and the latter were extracted with ether. The ethereal solution possessed a blue fluorescence, and on evaporation yielded a semi-solid residue, amounting to about 0·7 per cent. of the original oil. On extracting this residue with light petroleum a solution with a deep blue fluorescence was obtained, which yielded needle-shaped crystals. This acid, after recrystallisation from the same solvent, melted at 179°; it had a strong, unpleasant odour, and was soluble either in dilute hydrochloric acid or in dilute sodium hydroxide. The

substance thus behaved like an amino-acid, and agreed in its general characters and melting point with methylanthranilic acid. It was probably present in the oil in the form of its methyl ester.

Isolation of a New Ketone, $C_{24}H_{28}O_4$.

When the portion of the oil which boiled above 135°/20 mm., or above 270° under the ordinary atmospheric pressure, was left for a few days, colourless crystals separated. These were removed by filtration, and on cooling the filtrate to −10° a further quantity was obtained, the total amount thus secured being about 8 per cent. of the weight of the original oil. After repeated recrystallisation from alcohol, the substance had a constant melting point of 102° and $[\alpha]_D^{22} + 198°20'$ in solution in chloroform. It forms large, transparent, diamond-shaped crystals, which are colourless when freshly prepared, but soon become yellow, and gradually assume a brown colour. The crystalline substance is almost inodorous, but in dilute alcoholic solution it possesses the peculiar characteristic odour, somewhat resembling crushed ivy leaves, which can be readily detected in the oil itself. The compound is insoluble in water, but readily soluble in alcohol, ether, or benzene. It is highly unsaturated, and readily combines with about twice its weight of bromine. It does not unite with sodium sulphite or with sodium hydrogen sulphite.

Attempts to oxidise the ketone with alkaline potassium permanganate solution were unsuccessful, the compound being recovered unchanged, whilst, when treated with chromic acid, the substance was completely decomposed:

0·1800 gave 0·4997 CO_2 and 0·1192 H_2O. C = 75·70; H = 7·36.*

C_6H_7O (or $C_{24}H_{28}O_4$) requires C = 75·8; H = 7·4 per cent.

When the substance was heated with hydriodic acid according to Zeisel's method, no evidence of the presence of methoxy- or ethoxy-groups could be obtained.

Preparation of the Oxime.—In order to prepare the oxime a 10 per cent. solution of the compound in alcohol was treated with an equal quantity of hydroxylamine hydrochloride and a slight excess of sodium hydroxide, each dissolved in a small quantity of water, and the mixture was heated for two hours on the water-bath. On pouring the product into water a *hydroxylamine-oxime* was precipitated. This substance was insoluble in water, and only sparingly soluble in alcohol or ether; it separated from solutions in the latter solvents in small, hard, white crystals, which melted at 184°. When the hydroxylamine-oxime was shaken with water slightly acidified with hydrochloric acid, the excess

* A second analysis gave C = 75·68; H = 7·38.

of hydroxylamine was removed, and the free oxime produced. The *oxime*, $C_{24}H_{28}O_3{:}NOH$, is insoluble in water, but is readily soluble in alcohol, ether, or benzene, and separates from these solvents in white, crystalline tufts melting at 166°. It is fairly easily hydrolysed by hydrochloric acid, and advantage was taken of this property as a means of determining its composition. A weighed quantity of the oxime was dissolved in a mixture of alcohol (3 parts), concentrated hydrochloric acid (1 part), and water (1 part), and the solution was boiled for three-quarters of an hour under a reflux condenser. The mixture was then diluted with water and titrated with $N/10$-iodine solution in the presence of excess of magnesia in order to estimate the hydroxylamine:

I. 0·1 gram of the oxime required 4·9 c.c. $N/10$-iodine solution.
II. 0·1 „ „ „ 5·1 „ „ „

or, as the mean of the two experiments, 0·1 gram required 5·0 c.c., which is equivalent to 0·00775 gram :NOH, or 7·75 per cent.

$C_{24}H_{28}O_3{:}NOH$ requires :NOH = 7·85 per cent.

Acetylation and Benzoylation Experiments.—When the ketone was boiled for an hour with acetic anhydride in the presence of sodium acetate, acetylation did not take place, and on pouring the mixture into water the unaltered substance was precipitated.

On treating the compound with benzoyl chloride and alkali hydroxide by the Schotten-Baumann process, a *benzoyl* derivative was produced as a cream-coloured powder, which was almost insoluble in alcohol or ether, and melted and decomposed above 260°; it yielded benzoic acid on hydrolysis.

Action of Alcoholic Alkali Hydroxide on the Ketone.—When a solution of the ketone in $N/2$-alcoholic potassium hydroxide was heated to boiling, a solid *substance* separated, whilst the amount of alkali hydroxide did not undergo any diminution. The substance was obtained as an amorphous powder; it melted and decomposed at about 200°, and was sparingly soluble in ether or alcohol, rather more so in ethyl acetate, and extremely soluble in chloroform. It could not be obtained from any of these solvents in a crystalline form, and on evaporating a solution in chloroform, a viscous, resinous residue was produced.

Examination of the Heavy Oil.

The heavy portion of the oil, amounting to 7 per cent. of the total yield, was, when first distilled, a dark brown, viscous liquid with an odour recalling that of crushed ivy leaves. It gradually became semi-solid, however, owing to the separation of a crystalline substance, which proved to be the ketonic compound, melting at 102°. After the crystals had been removed, the residual oil

appeared to consist of a solution of the ketone in certain liquid constituents of high boiling point, probably sesquiterpenes.

From the results of this investigation the conclusion may be drawn that the volatile oil of the tubers of *Kaempferia Ethelae* has approximately the following composition:

	Per cent.
Terpenes, including dipentene and probably pinene	21·8
Cineole	17·2
Ketonic compound, m.p. 102°.....	13·0
Alcohols, including linalool.....	11·2
Esters, chiefly or entirely methyl methylanthranilate...	1·3
Phenols	0·5
Acids, chiefly or entirely acetic acid.....	0·1
Residue, probably chiefly sesquiterpenes.....	34·9

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XXXVII.—*Researches on Silicon Compounds. Part VIII. The Preparation and Constitution of Silico-Oxalic Acids, and the Action of Methyl and Ethyl Alcohols on Trisilicon Octachloride.*

By GEOFFREY MARTIN.

SILICO-OXALIC acid, $(SiO_2H)_x$, has hitherto been prepared by two methods only, by neither of which can it be obtained pure.

The first method is that described by Friedel and Ladenburg (*Annalen*, 1880, **203**, 250), and consists in decomposing disilicon hexaiodide, Si_2I_6, with water, when the following change takes place:

$$Si_2I_6 + 4H_2O = Si_2O_4H_2 + 6HI.$$

However, the product contains, according to Gattermann and Weinlig (*Ber.*, 1894, **27**, 1943), only 86 per cent. of silico-oxalic acid.

The second method, discovered by Gattermann and Weinlig (*loc. cit.*) consists in decomposing disilicon hexachloride, Si_2Cl_6, by means of atmospheric moisture at the temperature of melting ice:

$$Si_2Cl_6 + 4H_2O = Si_2O_4H_2 + 6HCl.$$

Even under the most favourable conditions Gattermann and Weinlig did not succeed in obtaining a product of more than 96—97 per cent. purity.

The displacement of iodine or chlorine atoms (which are directly attached to the silicon atoms) by hydroxyl groups evidently causes such a shock to the unstable molecule that a certain amount of decomposition seems inevitable, no matter how carefully the displacement is carried out. It therefore occurred to the author that a considerably purer specimen of silico-oxalic acid would be obtainable if one proceeded from a derivative of disilicon hexachloride, Si_2Cl_6, in which the oxygen atoms were already attached to the silicon atoms, as this would not involve such a deep-seated change as is represented by the displacement of a chlorine atom by hydroxyl.

When hexaethylsilicoethane, $Si_2(OEt)_6$ (T., 1914, **105**, 2871), is treated with water, hydrolysis to pure silico-oxalic acid slowly proceeds in the cold. It is possible by this method to obtain silico-oxalic acid (99—100 per cent.), the action being represented by the equation $Si_2(OEt)_6 + 4H_2O = Si_2O_4H_2 + 6EtOH$.

The production of silico-oxalic acid by this method also settles conclusively the question of its constitution. For this substance there have been proposed the two constitutional formulæ:

O:SiH·O·O·SiH:O and O:Si(OH)·Si(OH):O.
(I.) (II.)

Both formulæ explain fairly well the chemical behaviour of the substance, and up to the present time no clear proof has been given as regards which formula is to be preferred. The subject has attained some importance recently, since in Abegg's "Handbuch der anorganischen Chemie," 1909, **3**, II., p. 351, the formula I is chosen as being the more probable, because it explains very naturally the tendency of the substance to decompose into silica, and it brings the constitution of silico-oxalic acid into line with that of the anhydride of silico-formic acid, which is usually supposed to be O:SiH·O·SiH:O.

However, formula I cannot be correct, because, as shown below, silico-oxalic acid can be produced quantitatively by the following series of reactions:

$$Cl_3Si{\cdot}SiCl_3 \xrightarrow{EtOH} (EtO)_3Si{\cdot}Si(OEt)_3 \xrightarrow{H_2O} (HO)_3Si{\cdot}Si(OH)_3 \xrightarrow{-2H_2O} HO{\cdot}SiO{\cdot}SiO{\cdot}OH.$$

The hydrolysis of hexaethoxysilicoethane, $Si_2(OEt)_6$, into silico-oxalic acid, $Si_2O_4H_2$, proceeds smoothly, without any violent action or the evolution of appreciable amounts of heat, so that it is out of the bounds of probability that any intramolecular rearrangement has taken place during the process of hydrolysis.

The above reasoning does not exclude the possibility that silico-oxalic acid is a cyclic silicon compound, a view which the author will develop in a later communication.

The success of the method of preparing silico-oxalic acid by the hydrolysis of hexaethoxysilicoethane, $Si_2(OEt)_6$, by means of water led the author to attempt to obtain mesosilico-oxalic acid,

$$HO_2Si{\cdot}Si(OH)_2{\cdot}SiO_2H,$$

by preparing octaethoxysilicopropane, $Si_3(OEt)_8$, and decomposing this with water. For this purpose trisilicon octachloride, Si_3Cl_8, was treated with ethyl alcohol in a manner similar to that employed by the author in the preparation of hexaethoxysilicoethane (*loc. cit.*).

However, instead of obtaining the required substance, it was found that an almost complete decomposition of the molecule occurred, with the evolution of heat, and among the distillation products there was isolated tetraethoxysilicomethane, $Si(OEt)_4$.

A similar attempt to prepare the methoxy-derivative, $Si_3(OMe)_8$, by treating trisilicon octachloride, Si_3Cl_8, with methyl alcohol led to a similar but not so extensive decomposition of the molecule. Evidently merely treating trisilicon octachloride with methyl or ethyl alcohol is sufficient to sever the chain of three directly linked silicon atoms, ·Si·Si·Si·, in the molecule of trisilicon octachloride, producing decomposition products which do not contain more than two directly linked silicon atoms in the molecule, as was proved by estimating the amount of hydrogen evolved with potassium hydroxide.

This fact furnishes a striking illustration of the decrease in stability occasioned by an increase in the number of directly linked silicon atoms. This is obvious when it is recalled that hexaethoxysilicoethane, $Si_2(OEt)_6$, containing only two directly united silicon atoms, can be produced directly from disilicon hexachloride, Si_2Cl_6, merely by treating with alcohol, and that it will bear distillation under diminished pressure without decomposition, whereas the corresponding compounds, having the formulæ $Si_3(OEt)_8$ and $Si_3(OMe)_8$, are so unstable that they cannot be prepared by a similar method, and will not bear distillation.

The marked superiority of stability of disilicon hexachloride, Si_2Cl_6, over trisilicon octachloride, Si_3Cl_8, has already been commented upon in a previous paper (T., 1914, **105**, 2838), whilst specimens of mesosilico-oxalic acid, $HO_2Si{\cdot}Si(OH)_2{\cdot}SiO_2H$, prepared by the author by decomposing trisilicon octachloride by atmospheric moisture, were certainly more explosive than similar specimens of silico-oxalic acid.

Experimental.

Action of Water on Hexaethoxysilicoethane, $Si_2(OEt)_6$.

1·60 Grams (1 mol.) of hexaethoxysilicoethane were placed in a small weighing bottle, and 1·6 c.c. (18 mols.) of cold water were run in from a burette. The oil was slowly decomposed by the water, a white substance gradually separating out, and a very feeble development of heat was observed. After ten minutes the whole had set to a stiff paste. The mixture was kept for forty-eight hours, and was then collected and washed with a little water. The washings were tested for ethyl alcohol by means of the iodoform reaction, and the presence of a large amount was proved, showing that the action of water was a hydrolysing one. A white, amorphous solid was left on the filter, which, after washing with cold water and drying overnight in a vacuum over sulphuric acid, amounted to 0·595 gram, so that 1 gram of hexaethoxysilicoethane yielded 0·37 gram. Another experiment gave 0·372 gram. According to the equation:

$$Si_2(OEt)_6 + 4H_2O = Si_2O_4H_2 + 6EtOH,$$

1 gram of hexaethoxysilicoethane should yield 0·375 gram of silico-oxalic acid.

The silico-oxalic acid obtained in this way dissolved in aqueous potassium hydroxide to a clear solution, with the evolution of hydrogen. It exploded feebly when scratched, rubbed, or suddenly heated. The hydrolysis was complete in the cold, because on boiling the substance with water in a test-tube fitted with a reflux condenser, no alcohol could be detected in the filtrate. This result was confirmed by some other experiments.

Experiments were now carried out in order to see whether the same final product was obtained when hexaethoxysilicoethane was hydrolysed by means of hot water; 0·9086 gram of the substance was placed in a crucible, treated with a little water, allowed to remain overnight, then heated with water on the water-bath, and finally evaporated to dryness. The drying was completed in the steam-oven. The solid finally obtained weighed 0·3391 gram. Hence 1 gram of hexaethoxysilicoethane gave 0·373 gram. According to theory (see above equation) the yield should be 0·375 gram.

This experiment proved that heating with water does not noticeably affect the nature of the product. Also that the product can be dried in the steam-oven without a noticeable alteration in weight. However, as will be seen immediately, the silico-oxalic acid produced in the cold is considerably purer (as judged by the volume of hydrogen evolved by the action of potassium hydroxide) than the similar product produced by means of hot water.

This is only to be expected from the unstable nature of silico-oxalic acid.

Analysis of the Product of Hydrolysis.—The identity with silico-oxalic acid of the white solid produced by the hydrolysis of hexaethoxysilicoethane was proved by analysis and by measuring the hydrogen evolved with potassium hydroxide.

The silicon was determined as follows: First of all a specimen of silico-oxalic acid was prepared by treating hexaethoxysilicoethane with cold water, and drying in a vacuum over sulphuric acid.

Next the substance was placed in a platinum crucible and covered with ammonia solution. This decomposed the silico-oxalic acid, evolving hydrogen. The addition of ammonia was necessary because a direct heating of the solid may cause a mild explosion, with resulting loss of silica. When the hydrogen ceased to be evolved the whole was evaporated to dryness on the water-bath, and the white residue was ignited:

0·1012 gave 0·0994 SiO_2. Si = 46·12.

$Si_2O_4H_2$ requires Si = 46·15 per cent.

A combustion with copper oxide showed that the substance contained no appreciable amount of carbon, proving that the displacement of the ethoxy-groups was complete.

The volume of hydrogen evolved with potassium hydroxide was determined in the usual way by means of a Lunge nitrometer, using 50 per cent. potassium hydroxide solution, and warming towards the end of the reaction, when a clear solution was effected:

0·1272 gave 24·8 c.c. H_2 (moist) at 19° and 770 mm., whence
1 gram gave 181·0 c.c. H_2 (dry) at N.T.P.

According to theory, 1 gram of pure silico-oxalic acid, $Si_2O_4H_2$, should evolve 182·7 c.c. H_2 (dry) at N.T.P.; hence the specimen of silico-oxalic acid thus obtained was of 99 per cent. purity.

The best specimens of silico-oxalic acid obtained by Gattermann and Weinlig's process of decomposing disilicon hexachloride with water never exceeded 96—97 per cent. purity.

Specimens of silico-oxalic acid, prepared by hydrolysing hexaethoxysilicoethane with hot water, or after being boiled for some time with water, evolved considerably less hydrogen—as is to be expected from the unstable nature of silico-oxalic acid. Even if the product be rubbed or pressed, a certain amount of decomposition may ensue; for example, two specimens of silico-oxalic acid, obtained by decomposing hexaethoxysilicoethane by hot water, evolved, when treated with potassium hydroxide, 175 c.c. and 167 c.c., respectively, of dry hydrogen per gram weight. These numbers correspond respectively with 96 and 91 per cent. of

silico-oxalic acid. The last specimen had actually been boiled with water before analysis.

The details given above show that by this method of preparation almost pure silico-oxalic acid can be obtained, provided that ordinary precautions are taken, and that the temperature is kept low.

Properties.—Pure silico-oxalic acid is a snow-white, amorphous powder, insoluble in the usual mineral acids, with the exception of hydrofluoric acid, which decomposes it. Alkalis and ammonia decompose it, causing the evolution of hydrogen. Pressure, friction, or sudden heating usually cause its explosive decomposition, and the purer the substance is the more liable is it to decompose. However, the explosion does not readily spread from particle to particle; for example, if some of the amorphous powder is spread thinly over the bottom of a glass dish and part touched with a hot glass rod, the particles touched will explode, but the explosion usually confines itself to the immediate neighbourhood of the hot glass.

When freshly prepared and dried in a vacuum over sulphuric acid it is very hygroscopic.

Action of Ethyl Alcohol on Trisilicon Octachloride.—The favourable results obtained by the above method of preparing silico-oxalic acid led the author to see whether mesosilico-oxalic acid, $HO_2Si{\cdot}Si(OH)_2{\cdot}SiO_2H$, could be obtained of great purity by the similar method of first preparing octaethoxysilicopropane, $Si_3(OEt)_8$, by acting on trisilicon octachloride with alcohol, and then hydrolysing the product with water.

In order to prepare octaethoxysilicopropane, 23 grams of trisilicon octachloride were placed in a flask fitted with a reflux condenser and a calcium chloride tube, and 50 c.c. of alcohol (99·8 per cent.) were gradually added. A vigorous action took place, much hydrogen chloride being evolved.

Seeing that great cold is produced when excess of alcohol is added to disilicon hexachloride (hoar frost actually collecting on the sides of the flask, compare T., 1914, **105**, 2861), it was expected that an even more pronounced degree of cold would be experienced by treating the more unstable trisilicon octachloride in the same way. To the author's surprise, however, although at first the mixture became moderately cold, yet the temperature soon began to rise as the action proceeded, and finally the contents of the flask became quite hot.

This, as will immediately be seen, was due to the decomposition of the chain of three directly linked silicon atoms in the trisilicon octachloride. From all grounds of analogy the production of a

compound of formula $Si_3(OEt)_8$ should have been attended with the absorption of more heat than the formation of a compound of formula $Si_2(OEt)_6$.

When the evolution of hydrogen chloride had almost ceased, the liquid was warmed on the water-bath and left overnight. Since in the case of the preparation of hexaethoxysilicoethane, $Si_2(OEt)_6$, the complete displacement of the chlorine by ethoxy-groups proceeded only slowly, it was deemed advisable to add a further 20 c.c. of alcohol and warm once more. Finally, the alcohol was distilled off. The distilled alcohol contained much hydrogen chloride and a small amount of some volatile silicon compound, since on diluting with water a slight milkiness occurred.

The liquid left in the flask was now subjected to fractional distillation under diminished pressure. The distillation began about 77°/18 mm., and the thermometer rose slowly but steadily up to 220°, at which point the distillation was stopped.

A small quantity of viscid oil remained in the flask. The distillates were colourless oils free from chlorine, and three fractions were collected: (1) b. p. 77—90°/18 mm.; (2) 90—145°/18 mm.; (3) 145—220°/18 mm. It was evident that the product was a complex mixture, and that the reaction:

$$Si_3Cl_8 + 8EtOH = Si_3(OEt)_8 + 8HCl$$

had not taken place. The separate fractions were fractionally distilled, and the fraction of lowest boiling point was proved to consist almost entirely of tetraethoxysilicomethane, $Si(OEt)_4$. It evolved no hydrogen with potassium hydroxide (proving the absence of directly linked silicon atoms; see *Ber.*, 1912, **45**, 2097; 1913, **46**, 3289), and was completely hydrolysed to silicic acid by water (0·2164 gave 0·0633 SiO_2 on decomposing with concentrated sulphuric acid. Si = 13·7. $Si(OEt)_4$ requires Si = 13·6 per cent.). The fact that a considerable proportion of tetraethoxysilicomethane was thus obtained showed that there had occurred a very considerable disruption of the ·Si·Si·Si· chain present in the trisilicon octachloride when the latter was treated with alcohol.

The fractions of higher boiling point were also re-distilled, but it was impossible to isolate any fraction of constant boiling point, and with each successive distillation a large portion of the liquid to be distilled became converted into liquids of higher boiling points—evidently polymerised or complex decomposition products. This was made certain by analysing the products; for example, the fraction collected between 90° and 145°/18 mm. contained Si = 17·46, and 1 gram, when treated with potassium hydroxide, evolved about 18 c.c. of hydrogen.

The fraction collected between 145° and 220°/18 mm. con-

tained Si = 20·2, and 1 gram, when treated with potassium hydroxide, evolved 24·9 c.c. of dry hydrogen at N.T.P.

Since octaethoxysilicopropane, $Si_3(OEt)_8$, requires Si = 19·1 and 1 gram should evolve with potassium hydroxide 100·8 c.c. of hydrogen at N.T.P., the above analyses serve to show that an almost complete decomposition of the octaethoxysilicopropane had occurred, either before or during the process of distillation.

It was thought, therefore, that since octaethoxysilicopropane would certainly not bear distillation under diminished pressure, better results would be obtained by simply treating the trisilicon octachloride with alcohol, without attempting to isolate the product by distillation.

For this purpose 12·3 grams of pure silicon octachloride were placed in a distilling flask provided with a reflux condenser, and 23 grams of pure ethyl alcohol were gradually added.

After the vigorous action which had set in had subsided, the liquid was warmed on the water-bath to expel the excess of hydrochloric acid. Traces of a volatile silicon compound escaped with the hydrogen chloride, because an incrustation collected at the top of the reflux condenser. The excess of alcohol was removed by distilling on the water-bath, and twice there was added about 30 c.c. of alcohol, which was then distilled off in order to expel traces of dissolved hydrogen chloride. During the distillation of the alcohol a current of dry hydrogen was passed through the liquid in order to help the removal of the dissolved hydrogen chloride. The liquid so obtained was almost clear, and was rendered quite clear by filtering through a layer of recently dried asbestos. When thrown into water, it floated on the surface in oily drops, which were only slowly decomposed with the formation of a white solid. The liquid, when filtered from the solid and acidified with nitric acid, did not give a precipitate with silver nitrate. Since no trace of chlorine could be detected, and since the liquid evolved hydrogen with potassium hydroxide, it was thought that the action $Si_3Cl_8 + 8EtOH = Si_3(OEt)_8 + 8HCl$ had proceeded to completion. Consequently an analysis was made.

The silica was determined in the usual way by decomposing with concentrated sulphuric acid:

0·2824 gave 0·1044 SiO_2. Si = 17·4.

1·0 „ , with potassium hydroxide, only 42·3 c.c. H_2 (dry) at N.T.P.

Since the formula $Si_3(OEt)_8$ requires Si = 19·1, and 1 gram should evolve with potassium hydroxide 100·8 c.c. of dry hydrogen, the above figures show that the rupture of the molecule of octaethoxysilicopropane had proceeded to nearly 60 per cent. Attempts

to isolate octaethoxysilicopropane were, therefore, abandoned, as, with the means at the author's disposal, there seemed no prospect of isolating it in a pure condition.

Action of Methyl Alcohol on Trisilicon Octachloride.—It was thought that possibly the methoxy-compound, $Si_3(OMe)_8$, would prove more stable than the ethoxy-compound, and so attempts were made to prepare it. 18·42 Grams of trisilicon octachloride were treated with 44 grams of pure methyl alcohol (purified by metallic calcium and silver oxide). The action proceeded with development of heat and the evolution of hydrogen chloride, exactly as was the case with ethyl alcohol. The liquid was warmed on the water-bath in order to complete the action, and the excess of alcohol was distilled off on the water-bath in a current of dry hydrogen. There finally remained, after the complete removal of the alcohol, 12·2 grams of a colourless liquid. This was subjected to fractional distillation under 14 mm. pressure. The temperature rose slowly from 90° to 140°/14 mm., whilst the liquid slowly distilled uniformly in drops. At the last temperature about one-third of the liquid remained as a viscid oil. It was evident that no fraction of constant boiling point could be isolated, and that a complex mixture of decomposition products had resulted.

Thus the distillate, boiling between 90° and 170°/13 mm., was analysed in the usual way:

0·2681 gave 0·1381 SiO_2. Si = 24·2.

1 gram gave with potassium hydroxide only 36·6 c.c. H_2 (dry) at N.T.P.

$Si_3(OMe)_8$ requires Si = 25·5 per cent., and 1 gram should yield with potassium hydroxide 134·5 c.c. H_2 (dry) at N.T.P.

Hence the chains of directly united silicon atoms, as judged by the evolution of hydrogen with potassium hydroxide, were almost completely destroyed.

The decomposition had not proceeded so far in the oil which had not distilled. This was found to contain Si = 27·6, and 1 gram gave 68·2 c.c. H_2 (dry) with potassium hydroxide.

When treated with water the oils were decomposed with the formation of white solids, which evolved hydrogen with potassium hydroxide and ammonia, and were readily combustible. When the oils were treated with ammonia solution they were violently decomposed, with the evolution of hydrogen and formation of silicic acid.

The preceding experiments indicated that there seems little prospect, with the means at the author's disposal, of preparing a pure specimen of octamethoxysilicopropane, $Si_3(OMe)_8$, as this substance, if formed at all, will not bear distillation.

This great instability of derivatives containing a chain of three silicon atoms directly linked led the author to investigate the relative stability of mesosilicic acid, $HO_2Si{\cdot}Si(OH)_2{\cdot}SiO_2H$, and silico-oxalic acid, $HO_2Si{\cdot}SiO_2H$. Thin layers of these acids were prepared by pouring a little of the chlorides Si_3Cl_8 and Si_2Cl_6 on to a smooth wooden surface and exposing to atmospheric moisture for some hours. On testing these layers by means of a hot wire or by friction, it was found that the mesosilico-oxalic acid exploded more readily than the silico-oxalic acid. The film of mesosilico-oxalic acid would, when rubbed, often blaze up like gunpowder, whereas the effect was much less pronounced with silico-oxalic acid.

The expenses of this investigation were defrayed from a grant by the Senate of London University from the Dixon Fund, and also by a grant from the Research Fund Committee of the Chemical Society, for which the author wishes to express his best thanks.

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[*Received Jan. 16th*, 1915.]

XXXVIII.—*The Velocities of Flame in Mixtures of Methane and Air. Part II.*

By Albert Parker.

The progress of flame in mixtures of methane and air in various proportions has previously been examined by the author in conjunction with Mr. A. V. Rhead (T., 1914, **105**, 2150). Measurements of the velocities of flame in these mixtures were made between different points in tubes of copper, lead, iron, and glass of approximately 2·5 cm. diameter, in order that the effect of the material could be observed; the effect of a bend in the explosion tube was also studied. The firing agent employed consisted of a 3 mm. single break-spark produced from a weak Ruhmkorff coil by screwing up the hammer break of the primary coil, and rapidly breaking the contact by movement of a mercury switch.

It was found that in tubes of a given diameter the initial velocity of explosion varies with the material of the tube; it is less in tubes possessing a high conductivity for heat.

The maximum initial velocity is possessed by a mixture containing 10 per cent. of methane, the rate of propagation of which in a glass tube of 2·5 cm. was found to be 70 cm. per second. The

initial velocity then falls with change of methane content, moving towards zero at 4·5 and 13·1 per cent.

In the same paper reference was made to the detailed researches of Mallard and Le Chatelier as outlined in the *Bull. Soc. chim.* (1883, [ii], **39**, 369). A curve of initial velocities of methane–air mixtures (measured by these authors) was also given.

Since the publication of the results obtained by A. V. Rhead and the author, an account of a similar investigation by R. V. Wheeler has appeared in the Society's Transactions (T., 1914, **105**, 2606). In an addendum to this paper, Wheeler criticises our work in the following words:

"It is surprising to find that these authors are apparently unacquainted with Mallard and Le Chatelier's complete researches dealing with the 'uniform' and 'vibratory' movements during the propagation of flame in gaseous mixtures contained in glass tubes, as outlined in the present paper. Their results are interesting in that they emphasise the necessity, pointed out by Mallard and Le Chatelier, of employing tubes of ample diameter when conducting experiments of this nature; the tubes they used were of too small a diameter to enable them to determine either the true character of the speed-percentage curve or the limits of inflammability."

The complete researches of Mallard and Le Chatelier referred to by Wheeler are described in their well-known publication in the *Annales des Mines* (*Mémoires*, 1883, [viii], **4**, 274), which is a more detailed account of the experiments outlined in their five less-known memoirs in the *Bull. Soc. chim.* of the same year. The fourth of these memoirs, "Vitesse de propagation de la flamme," is the one with which we are directly concerned, and it is the author's intention to explain briefly why he and Rhead (whether rightly or wrongly) deliberately quoted the results presented to the Société chimique de Paris, in preference to those published in the *Annales des Mines*.

In the *Bull. Soc. chim.* Mallard and Le Chatelier describe the various methods they employed in the measurement of the initial uniform velocities of propagation of flame in different mixtures. The first method was that of the "orifice en mince paroi," which had previously been used in similar work by Mallard (*Ann. des Mines*, 1875, [vii], **7**, 355). By this method the gaseous mixture was made to pass along a glass tube, the end of which was covered by a thin metal disk, in which the orifice had been pierced. The mixture was ignited at the end of the tube, and its velocity gradually diminished until a point was reached at which the flame commenced to travel back through the orifice. The initial velocity

of the flame was then considered to be equal to the rate of flow of the gas through the orifice.

By the other methods used the mixture was contained in a glass tube, and was fired from an open to a closed end, various means being employed to record the passage of the flame at different points.

Using an orifice of 1 cm. diameter, Mallard and Le Chatelier obtained the following initial velocities for mixtures of methane and air:

Volume of methane added to 100 volumes of air.	Velocity in cm. per sec.	Methane per cent. in resultant mixture.
8·2	27	7·6
8·6	29	7·9
9·5	35	8·7
9·9	40	9·0
11·6	58	10·4
13·3	48	11·7
14·2	32	12·4
14·9	25	12·9

The results as published in the *Bull. Soc. chim.* are given in the first two columns; the third column contains the calculated percentage of methane in the resultant mixtures. Mallard and Le Chatelier pointed out that the maximum velocity corresponds with 12·2 volumes of methane (that is, 10·86 per cent.), an amount considerably greater than 10·4 volumes (9·4 per cent.), which theoretically gives the most explosive mixture. These authors then studied the effect of the addition of nitrogen and carbon dioxide to a mixture of 11·67 volumes of methane and 100 volumes of air; that is, a mixture containing 10·4 per cent. of methane:

Volume of nitrogen added to 100 volumes of mixture.	Velocity in cm. per sec.	Methane per cent. in resultant mixture.
0	58	10·4
3·5	41	10·04
7·0	42	9·72
11·0	32	9·37
Volume of carbon dioxide added to 100 volumes of mixture.		
0	58	10·4
3·5	42	10·04
7·0	27	9·72
11·0	18	9·37

From these results it is concluded that mixtures with excess of nitrogen possess the same initial velocities as mixtures with air containing an equal amount of methane, but that carbon dioxide considerably reduces the velocity.

Mallard and Le Chatelier then give the results of experiments

with hydrogen–air mixtures, the compositions of which are also expressed as volumes of combustible gas added to 100 volumes of air.

The above experiments are also described in the *Ann. des Mines*. In addition, results are given which were obtained with methane mixtures fired from an open to a closed end of a glass tube 5 cm. in diameter, but most of the measurements were made by the "orifice" method, and not, as would appear from Wheeler's abstract, by the "tube" method. In fact, only *two* of the "tube" results are plotted in the curve given in the *Ann. des Mines* and reproduced in Wheeler's paper. The compositions of the mixtures used are expressed in the *Ann. des Mines* as percentages of combustible gas, and not as volumes added to 100 volumes of air. In the case of hydrogen–air mixtures the percentages given agree with those calculated from the figures in the *Bull. Soc. chim.*; but not so for methane. The same figures given in the *Bull. Soc. chim.* as volumes added to 100 volumes of air are quoted in the *Ann. des Mines* as percentages of methane in the final mixtures.

The following methane–air results are selected from the *Ann. des Mines*:

Methane per cent. in mixture.	Velocity in cm. per sec.
8·7	29
10·0	39
11·5	54
13·2	48
14·9	25

By substituting "volumes of methane added to 100 volumes of air" for "methane per cent.," the above results become almost identical with those published in the *Bull. Soc. chim.*, and evidently refer to the same experiments.

If we turn to the values given in the *Ann. des Mines* as the results of experiments on the influence of an excess of nitrogen or carbon dioxide, we find that the experiments were made by adding increasing amounts of nitrogen or carbon dioxide to a mixture of methane and air containing 11·65 "per cent." of combustible gas:

	Volume of inert gas added to one volume of above mixture.	Methane per cent. in resultant mixture.	Velocity in cm. per sec.
Nitrogen	0·5	8·0	42
	1·0	5·8	30
	1·4	4·7	19
Carbon dioxide	0·5	8·3	31
	1·0	5·8	16

This table obviously contains several errors. In the first place,

the numbers 8 and 8·3 in the middle column should be 7·8. Secondly, Mallard and Le Chatelier conclude from these results that the effect of adding nitrogen is the same as that of adding an equal volume of air. This conclusion could not possibly have been drawn from the above values, as they are far removed from the velocities of methane–air mixtures containing the same amount of methane, given either in the *Bull. Soc. chim* or in the *Ann. des Mines*; for example, an 8 per cent. methane–air mixture would have an initial velocity of 23 or 29 cm. per sec., as against 42 cm. per sec. for the mixture containing excess of nitrogen.

On comparing the two sets of values given by Mallard and Le Chatelier with the earlier work of Mallard, and the recent results obtained by Parker and Rhead, and by Wheeler, we find for the percentage compositions of the methane–air mixtures of maximum velocity:

Mallard. (*Ann. des Mines*).	Mallard and Le Chatelier. (*Bull. Soc. chim*).	Mallard and Le Chatelier. (*Ann. des Mines*).	Parker and Rhead.	Wheeler.
10·8	10·86	12·2	10	10

The first two values were obtained by the same method, and show remarkable agreement with one another. The difference between Mallard's value of 10·8 per cent. and that obtained in the recent investigations may be explained on the assumption that his methane contained impurities equivalent to 7·4 per cent. of air; 10·86 would require impurities equivalent to 7·8 per cent. of air. Such impurity appears a probable amount, but the value 12·2 would necessitate 18 per cent. of impurity, a most improbable quantity.

After consideration of the above points it seemed to us reasonable to conclude that the values presented to the Société chimique de Paris by Mallard and Le Chatelier were the correct results of their experiments.

In reply to Wheeler's criticism of the small diameters of the explosion tubes used by Rhead and the author, it is only necessary to point out that one of the main objects of the experiments was to determine the effect of the material of the tube on the initial velocities of flame. This could not have been so easily accomplished in tubes of larger diameter, since the effect would obviously have been much smaller. The authors were well aware of the influence of diameter when their paper was published, for they had previously made a number of experiments in tubes of diameters varying from 1 to 17 cm. These experiments have been continued, and are described in the present paper.

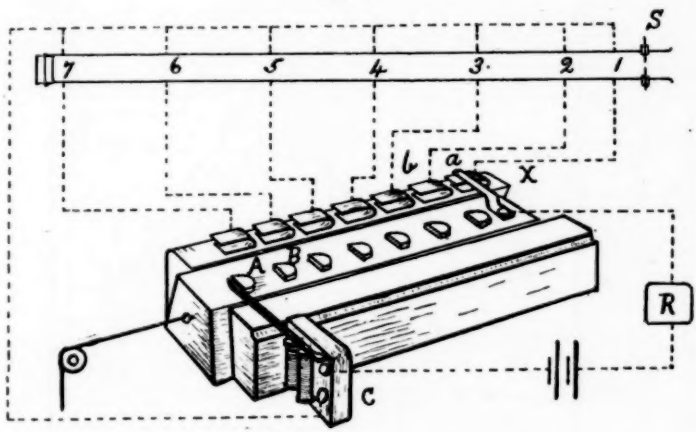
It was not claimed by Rhead and the author that the values

4·5 and 13·1 per cent. were the lower and upper limits, respectively, for methane; it was merely stated that the initial velocities of propagation of methane–air mixtures "moved towards" zero at 4·5 and 13·1 per cent.

Influence of Diameter of Tubes.

The initial velocities of propagation of flame in mixtures of methane and air have been measured in glass tubes varying in internal diameter from 1 to 9 cm. and in an iron tube of 17·5 cm. diameter. If it is assumed that in the largest diameter the effect of material would be inappreciable, the results obtained in the iron tube should be identical with the velocities of flame in a glass tube of the same dimensions.

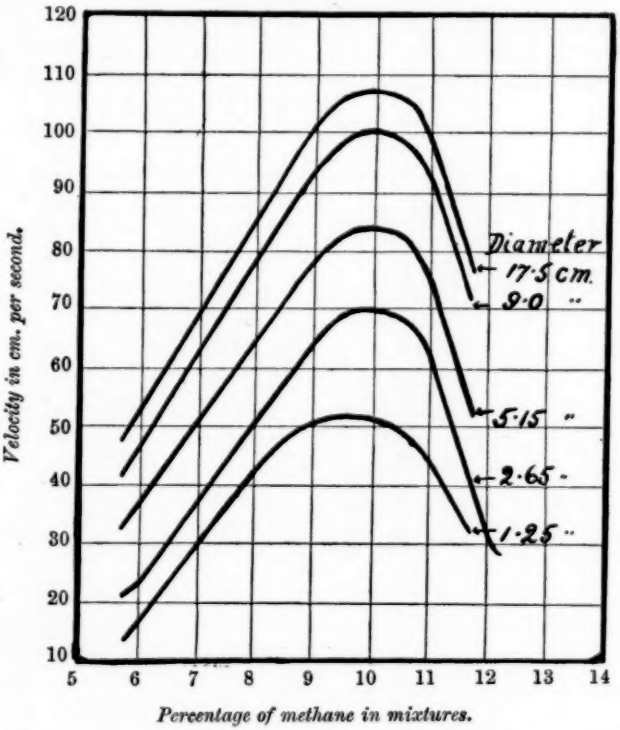
FIG. 1.



The method of measurement was practically the same as that previously described by Parker and Rhead; but an improvement was made in the recording apparatus by introducing an automatic commutator in place of the hand switch-board formerly used. The arrangement of the recording apparatus is shown in Fig. 1. The commutator, which somewhat resembles a slide-rule in shape, consists of a block of hard wood with a sliding centre-piece, which is moved along by means of a cord connected to a small leaden weight suspended from a pulley-wheel. This ensures a more constant pull on the centre-piece than would result from a coiled spring. The electrical circuits (represented by dotted lines) are completed by fixing thin Wood's metal bridges in the tube at the points 1, 2, 3, 4, 5, 6, and 7. The commutator, placed in the position shown in the diagram, allows a current to flow through

the fixed brass plate (*a*), the sliding contact *X*, the magnet *R* operating a style marking a revolving drum, and back through the commutator magnet *C*. By lowering an iron lever against the stud *A* the commutator magnet holds the sliding centre-piece in the starting position. The firing agent employed consisted of a 3 mm. single break-spark produced from the identical coil previously used by Parker and Rhead. As soon as the flame reaches 1, the metal bridge at this point is melted, releasing the recording

FIG. 2.



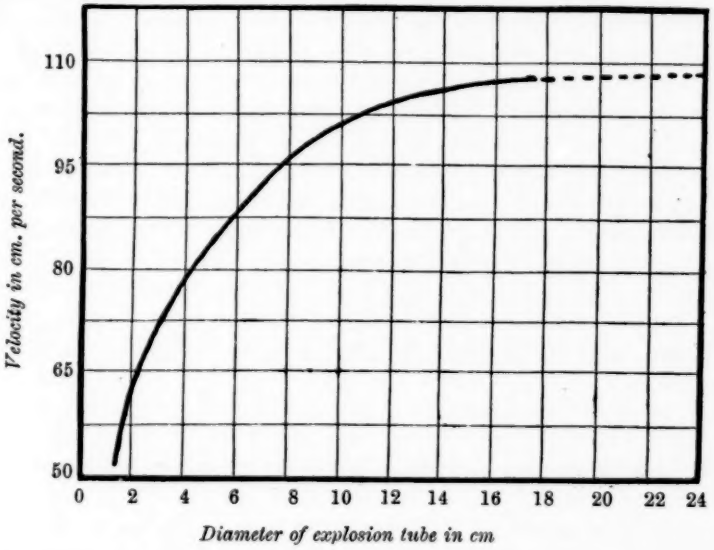
style and the lever of the commutator magnet *C*. This allows the centre-piece to move until the contact *X* reaches position (*b*), when the circuit is again completed through the second bridge. The second position is maintained by the lowering of the lever, which stops the stud *B* until the second bridge is melted, when the same cycle of operations is repeated.

In all the experiments carried out the mixtures were fired near an open end of the tube, the further end being closed. The spark was passed at approximately 15 cm. from the open end, and the

flame was allowed to travel 40 cm. before reaching the first bridge, after which a distance of from 50 to 70 cm. had to be traversed before the second bridge was reached. The tubes were each 5 metres long, and were of the following internal diameters in cm. glass: 1·25, 2·65, 5·15, 9·0; iron, 17·5.

Preparation of the Gaseous Mixtures.—The gases were mixed in a large graduated gas-holder over water which had previously been in contact with a mixture of the same composition. The capacity of the holder (180 litres) enabled one experiment to be carried out in each of the four glass tubes with the same mixture. A fresh mixture had to be made for each experiment in the iron tube.

FIG. 3.



Methane.—This gas was prepared by Campbell and Parker's method (T., 1913, **103**, 1292) from aluminium carbide and water; it was purified as described by these authors.

The mixtures examined contained amounts of methane varying from 5·7 to 12 per cent. Curves of the initial velocities of these mixtures are shown in Fig. 2, where percentages of methane are plotted against initial uniform velocities. It may be observed from these curves that the velocities increase considerably with the diameter of the explosion tube, and that the limiting diameter cannot be less than 17·5 cm. The probable value of the limiting diameter is most easily estimated by an examination of the curve shown in Fig. 3, where the initial velocities of a mixture containing

10 per cent. of methane are plotted against the diameters of the explosion tubes. From this curve it may be seen that a decrease in diameter has a considerable effect with tubes smaller than 15 cm. The limiting value is probably not much above 20 cm., but in a tube of this size the velocity is only 1 per cent. greater than in a tube of 15 cm. diameter.

It may be finally concluded from these experiments that in order to obtain the true values of the uniform velocities of propagation of flame in mixtures of methane and air, it is necessary to employ tubes of at least 15 cm. diameter.

Effect of Source of Ignition.

It is noticeable that the initial velocities of flame in mixtures of methane and air in glass tubes of 5 cm. diameter, as measured by Wheeler, are very much greater than the values obtained by the author; for example, for a mixture containing 10 per cent. of methane Wheeler gives a value of 113 cm. per second, whereas the author has found the velocity to be only 84 cm. per sec. This large difference cannot be attributed to experimental error; nor is it probable that it is due to the differences in purity of the methane used. (Wheeler prepared methane from natural fire-damp; it contained small quantities of carbon monoxide and ethylene.) The only remaining explanation appears to be that it is caused by some difference in the nature of the igniting spark. To test this explanation the following experiments have been carried out.

A methane–air mixture containing 10·09 per cent. of combustible gas was fired in a glass tube of 5·15 cm. diameter and 5·290 metres long, at a distance of 17 cm. from the open end. The flame was then allowed to travel 17 cm. before reaching the first bridge, after which a distance of 36·5 cm. had to be traversed before the second bridge was reached; the distance between the second and the third flame indicators was 79 cm. The spark-gap in each experiment was 3 mm.; the mixture was fired by a single break-spark and by the ordinary discharge from three different coils, denoted by *A*, *B*, and *C*. The coil *A* was used in all the experiments previously described.

Coil.	Type of spark.	Velocity in cm. per second between Bridges 1 and 2.	Velocity in cm. per second between Bridges 2 and 3.
A	Single-break	84·0	96·6
B	" "	87·6	101·3
C	" "	98·9	117·5
A	Series of sparks	87·3	104·7
B	" "	99·8	99·3
C	" "	95·8	105·4

From the above results it may be observed that a variation in the coil used has increased the initial velocity from 84 to 98·9 cm. per second. A variation in the type of spark used has been able to increase the velocity from 87·6 to 99·8 cm. per second. It is possible that with a still more powerful discharge an initial velocity of 113 cm. per sec. or even greater would have been obtained.

In conclusion, it may be pointed out that in order to obtain the normal initial velocities of flame in mixtures of methane and air, it is necessary that the source of ignition should give no impetus to the propagation. There is evidence that an electric spark induces a sharper initial inflammation in gas mixtures than other modes of ignition (for example, adiabatic compression, Dixon, Bradshaw, and Campbell, T., 1914, **105**, 2032), and it is possible that the initial inflammation induced by a spark will always travel above the "normal" velocity.

The above-described experiments were carried out in the Chemical Laboratories of the University of Manchester.

THE UNIVERSITY,
BIRMINGHAM.

[*Received Feb. 8th*, 1915.]

XXXIX.—*Condensation of Acetone and Benzaldehyde with Glycerol. Preparation of Glycerol α-Methyl Ether.*

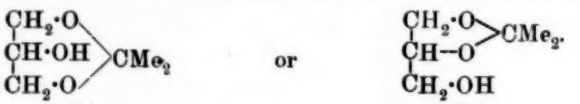
By JAMES COLQUHOUN IRVINE, JAMES LESLIE AULD MACDONALD (Carnegie Fellow), and CHARLES WILLIAM SOUTAR (Carnegie Scholar).

DEFINITE condensation compounds of polyhydric alcohols with acetone or benzaldehyde were first isolated in a pure condition by Fischer in the course of his earlier work on the sugar group (*Ber.*, 1894, **27**, 1536; 1895, **28**, 1167, 2496), and a considerable amount of research has been devoted to elucidate the structure of the substances thus produced. Owing to the extreme ease with which they are hydrolysed into their components (an instability which is frequently emphasised in the course of Fischer's papers) it is a matter of some difficulty to obtain direct experimental evidence

bearing on this question, but, in a recent review of the subject (Irvine and Paterson, T., 1914, **105**, 898), a general method for attacking the problem has been described, and applied to the case of mannitol triacetone.

The investigation described in the present communication was commenced several years ago, and had as its original object a study of the condensation of glycerol with acetone and benzaldehyde, evidence regarding the mechanism of this reaction being highly desirable in view of the nature of much of our recent work on the sugar group. In the earlier speculations on this subject it was recognised that, on account of its simple structure, glycerol is an extremely suitable compound on which to study the reaction in question, particularly as the hydroxyl groups do not differ widely in their reactivity, as is the case with reducing sugars. In addition, the complications encountered when condensation reactions of this type are conducted on active molecules are avoided in the case of glycerol.

As pointed out by Fischer, the *iso*propylideneglycerol (acetoneglycerol), formed by the interaction of glycerol and acetone in the presence of a catalyst, may possess either of two structures:



(I.) (II.)

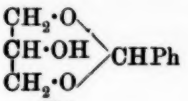
and no other alternatives need be considered in view of the results now described. From the fact that ethylene glycol fails to react with ketones whilst trimethylene glycol gives a positive result, the opinion has been expressed that the condensation involves hydroxyl groups attached to β-carbon atoms, and that, accordingly, *iso*propylideneglycerol should be represented by formula I. In the case of compounds formed with difficulty and hydrolysed with extraordinary ease, negative evidence of this nature is not conclusive, and ultimately the whole question of constitution was left quite open by Fischer, who termed the compound "acetone glycerol."

The methylation process offers a ready means of solving the problem. By methylation and subsequent hydrolysis, compounds constituted according to formulæ I and II should yield respectively β- or α-methyl ethers of glycerol:

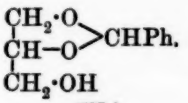
(III.) (IV.)

and a similar series of reactions should be applicable to benzylidene-

glycerol, and thus discriminate between the two alternative formulæ:



(V.)



(VI.)

On methylating *iso*propylideneglycerol by the silver oxide reaction, only one methyl group could be introduced, and the product consisted of the corresponding monomethyl ether (b. p. 57°/13 mm.). This result disposes of all structural schemes based on the reaction of acetone in the enolic form. Hydrolysis of the *iso*propylideneglycerol methyl ether yielded a glycerol monomethyl ether (b. p. 110—111°/13 mm.), and the main object of the research was accordingly directed to the allocation of the methyl group in this compound.

As described in the experimental part, this was by no means easy. C. F. Boehringer & Söhne have described and patented (D.R.-P. 1911, 226454) a glycerol methyl ether, but the description is imperfect, and the physical constants quoted are evidently rough approximations unsuitable for the purposes of comparison and identification of the compound. If, as appeared probable, the methylated glycerol obtained from *iso*propylideneglycerol corresponded with formula IV, the compound should be capable of resolution into active forms, and, with this object, we attempted to prepare an acid phthalate according to the method of Pickard and Kenyon (T., 1911, **99**, 45). In the case of a glycol, such as glycerol methyl ether, condensation with phthalic anhydride may give rise to several compounds, and we failed to isolate a pure product or to obtain satisfactory alkaloidal salts. An alternative process, which may yet be developed into a successful method for resolving glycols, was accordingly attempted. By condensing a *dl*-glycol with an active ketone two compounds should result, which should be separable by crystallisation. From these in turn, by the action of hydrolysts, the active glycols should be regenerated. In the case of glycerol methyl ether the desired reaction was carried out with *l*-menthone and with camphor, but in each case the products were liquids, and therefore useless for the particular object in view.

Recourse was therefore had to synthetical and decomposition methods of determining the constitution of the methylated glycerol. Starting from allyl iodide, the corresponding methyl allyl ether was prepared and converted into βγ-dibromo-α-methoxypropane. The replacement of the halogen atoms in this compound could not

be accomplished directly, but, by the action of silver acetate, the bromide was converted into βγ-diacetin methyl ether, which, on hydrolysis, yielded glycerol α-methyl ether. This product proved to be identical with the methylated glycerol obtained from *iso*propylideneglycerol, the constitution of the latter compound being thereby solved.

To obtain confirmatory evidence the glycerol methyl ether derived from the *iso*propylidene compound was heated with excess of anhydrous oxalic acid, and thus converted into methyl allyl ether, from which, in turn, the corresponding dibromide was prepared. The specimen isolated was identical in every respect with that obtained as described above from allyl iodide, the identity being established by boiling-point determinations at different pressures, the valuation of refractive index, density, and molecular refraction.

Constants of βγ-Dibromo-α-methoxypropane.

(*a*) Prepared from glycerol methyl ether.	(*b*) Prepared from methyl allyl ether.
b.p. ..... 83°/17 mm.	b.p. ..... 81°/16 mm.
n_D ... 1·5141	n_D ... 1·5143
D_4^{12} ..... 1·8320	D_4^{20} ..... 1·8329
M_D ... 38·17	M_D ..... 38·14 (Calc. 37·84).

The action of phosphorus haloids on glycerol methyl ether gave somewhat unexpected results. Phosphorus tribromide yielded a small quantity of a glycerol methyl ether bromohydrin, the constitution of which admits of two possibilities, but the main product of the reaction consisted of an acid phosphite of glycerol methyl ether bromohydrin. The exact nature of this compound has not yet been ascertained. A similar result was obtained when phosphorus pentabromide was used as the brominating agent, as, in this case also, the bulk of the glycerol ether was converted into an undistillable syrup containing combined phosphoric acid. The bromohydrin referred to above gave, on further treatment with phosphorus pentabromide, a good yield of βγ-dibromo-α-methoxypropane, but, as is usually the case in such reactions, the compound was contaminated with other derivatives containing a higher percentage of halogen, and thus the physical constants determined, although quite satisfactory, showed a slight variation from the standard values.

Other reactions of glycerol α-methyl ether, unconnected with its constitution, are described in the experimental part.

The proof that benzaldehyde condenses with glycerol in precisely the same manner as does acetone has been arrived at in the course

of a parallel series of reactions. Benzylideneglycerol, prepared by the process patented by Gerhardt (D.R.-P., 1913, 253083) gave, on methylation, benzylideneglycerol methyl ether, and this, on hydrolysis, was converted into a glycerol methyl ether, which proved to be identical with the form prepared through the agency of *iso*propylideneglycerol. A comparison of the physical constants of the glycerol ether derived from these different sources is given below:

Constants of Glycerol α-Methyl Ether.

(*A*) from *iso*propylidene glycerol.	(*B*) from benzylidene glycerol.
b.p. ..... 110–111°/13mm.	b.p. ..... 110–111°/13 mm.
n_D ... 1·4463	n_D ... 1·4461
D_4^{17} ..... 1·1197	D_4^{16} ..... 1·1190
M_D ... 25·26	M_D ... 25·27 (calc. 25·36).

As the methylated glycerols *A* and *B* are identical, it follows that benzylideneglycerol is represented by formula VI. Confirmatory evidence on this important point was obtained in the following manner: Glycerol methyl ether (*A*), derived from the *iso*propylidene compound, was condensed with benzaldehyde, thus forming benzylideneglycerol methyl ether. Similarly, in a parallel experiment, the methylated glycerol (*B*), obtained from the original benzylidene compound, was successfully condensed with acetone. The respective products proved to be identical with those previously prepared. This is shown in the following table of comparisons:

Constants of iso*Propylideneglycerol Methyl Ether.*

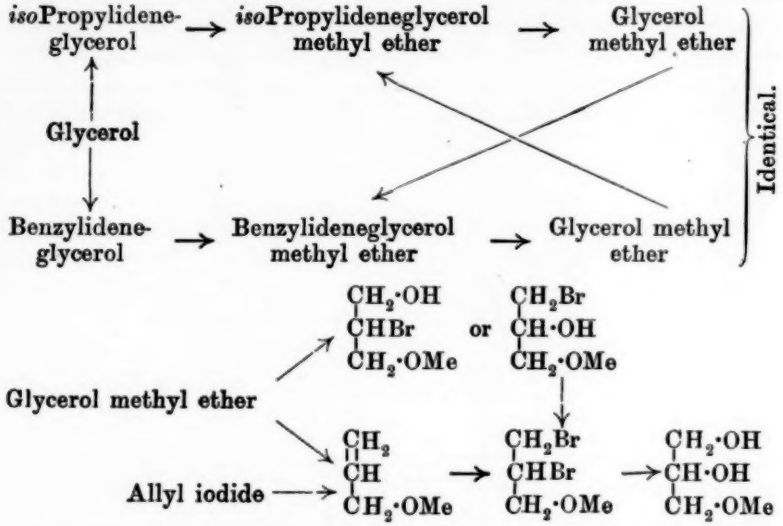
Derived from glycerol methyl ether (*A*).	Derived from glycerol methyl ether (*B*).
b.p. ..... 57°/13 mm.	b.p. ..... 56°/14 mm.
n_D ... 1·4177	n_D ... 1·4170
D_4^{15} ... 0·9900	D_4^{16} ... 0·9888
M_D ... 37·14 (Calc. 37·25).	M_D ... 37·13

Constants of Benzylideneglycerol Methyl Ether.

b.p. ..... 120°/2 mm.	b.p. ... 121°/1·6 mm.
n_D ... 1·5151	n_D 1·5170
D_4^{17} ..... 1·1253	D_4^{15} ... 1·1263
M_D ..... 52·00 (Calc. 52·12).	M_D ... 52·11

The schemes of reactions involved in the structural study and in

determining the constitution of glycerol α-methyl ether are summarised below:



It is, of course, possible that isomeric forms of *iso*propylidene-glycerol and of benzylideneglycerol exist in which the substituting residues are attached to the terminal carbon atoms (formulæ I and V), and, in this connexion, it may be noted that Harnitzki and Menschutkin (*Annalen*, 1865, **136**, 127) describe a "benzo-glycerol," which is apparently different from Fischer's "benzal glycerin." There is, however, little doubt that all the compounds described in the present communication are individual substances and not mixtures, as, in each preparation involving distillations, fractions were collected at frequent intervals even when the boiling point showed no change. In no case was there any appreciable variation in the refractive indices determined, and, as all the compounds now described have been prepared on several occasions without any irregularity being observed in the physical constants, it would appear that they are pure substances.

In all probability the methods described in the present paper will be capable of extension to the problems connected with the constitution of fats and of glycerophosphates. By alkylation of a mono- or di-glyceride, followed by hydrolysis, a glycerol dimethyl or monomethyl ether should result, and identification of the positions occupied by the alkyl groups would give direct evidence as to the structure of the parent compound. Moreover, much important research on the fats has shown that the hydrolysis of mixed glycerides by acids or enzymes can be controlled to give the inter-

mediate di- and mono-glycerides, so that the allocation of definite positions to the acyl groups in the glycerol residue should not be a matter of any great difficulty. It would, of course, be necessary, as a preliminary to such work, to determine the constants of all the possible methylated glycerols or to obtain derivatives from them suitable for the purposes of identification.*

Experimental.

Preparation of iso*Propylideneglycerol.*

The directions given by Fischer for the preparation of this compound were varied slightly, as we found it necessary to remove all traces of glycerol with the greatest care. Freshly distilled glycerol (100 grams) was shaken until dissolved with 650 c.c. of dry acetone containing 1 per cent. of hydrogen chloride. After twenty-four hours the solution was neutralised, first with lead carbonate and afterwards with silver carbonate, warmed with animal charcoal, and shaken with a large excess of calcium chloride. This treatment removed the uncombined glycerol, and the supernatant liquor was then decanted from the syrupy residue, the solvent removed, and the product fractionated under diminished pressure. In all, 327 grams of glycerol gave 290 grams of *iso*propylideneglycerol. B. p. 86·5°/13 mm., n_D 1·4383, D_4^{18} 1·0727, M_D 32·30 (calc., 32·51).

Alkylation of iso*Propylideneglycerol.*

To a solution of 80 grams of *iso*propylideneglycerol (1 mol.) in 280 grams of methyl iodide (3 mols.) 200 grams of silver oxide (1·5 mols.) were gradually added. The reaction, which was at first vigorous, was completed by boiling for six hours, and the product was then extracted with ether. On removal of the solvent and fractionation of the residual liquid under diminished pressure, 61 grams of *iso*propylideneglycerol methyl ether were obtained. This represents about the average yield, as, in three experiments, 242 grams of the *iso*propylidene derivative were, by this method, converted into 180 grams of the corresponding ether.

An additional quantity of the compound was obtained through the agency of methyl sulphate according to the method recently described for the methylation of sugar derivatives (Haworth, this

* With this object in view, it was our original intention to make a complete examination of the two glycerol monomethyl ethers and of the two corresponding dimethyl ethers, so that these compeunds could be used as reference substances in determining the structure of mixed glycerides and glycerophosphates. As my collaborators are, in the meantime, otherwise engaged, this extension of our work has been postponed, but we hope to return to the subject at a future date.—J. C. I.

vol., p. 8). Although an excellent yield of the desired product was obtained, it was contaminated with about 25 per cent. of glycerol methyl ether, which had been formed owing to slight hydrolysis in the last stages of manipulation. This impurity was, however, readily removed by fractional distillation, as the boiling points of the two products of the reaction lie far apart. B. p. 57°/13 mm., 75°/42 mm., n_D 1·4177, D_4^{15} 0·9900, M_D 37·14 (calc., 37·25).

Found: C = 57·48; H = 9·59.

$C_7H_{14}O_3$ requires C = 57·53; H = 9·59 per cent.

iso*Propylideneglycerol methyl ether* is a colourless, mobile liquid readily soluble in organic solvents, but sparingly so in water. The compound is hydrolysed with extreme ease, and, during its preparation and manipulation, care must be taken to exclude all traces of acids. Although Zeisel's method of estimating methoxyl groups cannot be applied to glycerol derivatives owing to the formation of *iso*propyl iodide in varying amount, the process may be modified so as to determine the methoxyl content of *iso*propylideneglycerol methyl ether with a fair degree of accuracy. The compound was, in the first place, decomposed with hydriodic acid at the minimum possible temperature (90°) until no further precipitation of silver iodide took place. Under these conditions only the alkyloxy-group reacted, but on raising the temperature to 130° *iso*propyl iodide was liberated, and a second quantity of silver iodide was collected:

Stage I. 0·1465 gave, at 90°, 0·2758 AgI.
Stage II. 0·1465 ,, on heating from 90° to 130°, 0·1511 AgI.
OMe determined at 90° = 24·8.
Apparent OMe determined between 90° and 130° = 13·6.

$C_7H_{14}O_3$ requires OMe = 21·2 per cent.

The above results, which are in agreement with those obtained by Lewkowitsch, emphasise the futility of the Zeisel process as a means of estimating glycerol.

Preparation and Methylation of Benzylideneglycerol.

The use of hydrogen chloride as a catalyst in the condensation of glycerol and benzaldehyde is unsatisfactory, and recourse was had to the method described by Gerhardt (*loc. cit.*). Pure re-distilled glycerol and benzaldehyde were used, and the reaction was conducted in an atmosphere of carbon dioxide. The benzylideneglycerol, which was obtained in satisfactory yield, boiled at 140°/0·07 mm., and solidified completely on cooling to a mass of pointed prisms, which melted initially at 65°. In the course of time, this melting point gradually increased until it reached 76°, but this

may have been due to some decomposition, and, in the subsequent methylation, freshly prepared material was used.

Owing to the instability of the compound, special precautions were necessary to avoid hydrolysis during the alkylation process, the methyl iodide employed being shaken with silver oxide and re-distilled before use, so as to remove traces of acid and of iodine. Seventy-five grams of the benzylidene compound (2 mols.) were dissolved in 290 grams of methyl iodide (10 mols.), and 145 grams of silver oxide (3 mols.) gradually added. After the vigorous spontaneous action ceased, the methylation was continued on the water-bath for eight hours, and the product, weighing 63 grams, isolated in the usual manner.

Benzylideneglycerol methyl ether boils at 121°/1·6 mm., and is insoluble in water, but readily dissolved by organic solvents generally, including light petroleum. Considerable difficulty was experienced in obtaining satisfactory analytical figures as the compound is hydrolysed at the ordinary temperature by the traces of acid present in laboratory air. All observations and analyses were therefore carried out immediately after distillation.

Found: C=67·83; H=7·23.

$C_{11}H_{14}O_3$ requires C=68·04; H=7·21 per cent.

n_D 1·5170; D_4^{15} 1·1263; M_D 52·11. Calc., 52·12.

No Zeisel determinations were attempted, owing to the irregularity of the process in the presence of glycerol.

Glycerol α-Methyl Ether.

Preparation from iso*Propylideneglycerol Methyl Ether.*—A 10 per cent. solution of *iso*propylideneglycerol methyl ether in 75 per cent. aqueous alcohol, containing 0·5 per cent. of hydrogen chloride, was boiled under a condenser for seventy minutes, after which the acid was removed by shaking successively with lead carbonate and silver carbonate. The filtrate, after the usual treatment with animal charcoal, was freed from alcohol by heating on a water-bath, and the aqueous solution of the hydrolysis product distilled. In this way, 75 grams of re-fractionated glycerol methyl ether boiling at 110°/13 mm. were obtained from 130 grams of the corresponding *iso*propylidene compound.

Found: C=45·25; H=9·45.

$C_4H_{10}O_3$ requires C=45·28; H=9·43 per cent.

0·1534 gave, by Zeisel's method, 0·2630 AgI between 100° and 105°, and, in addition, 0·2630 AgI between 105° and 130°.

No independent estimation of methoxyl was thus possible, but the total result is in agreement with the idea that glycerol methyl

ether is decomposed to give equimolecular proportions of methyl iodide and *iso*propyl iodide.

Glycerol α-methyl ether is a colourless, neutral liquid, readily soluble in water and in organic solvents. n_D 1·4463, D_4^{17} 1·1197, M_D 25·26. Calc., 25·36.

Preparation from Benzylideneglycerol Methyl Ether.—A 12 per cent. solution of the ether in 60 per cent. alcohol containing 0·6 per cent. of hydrogen chloride was heated on a boiling-water bath for seventy minutes. Thereafter, the alcohol was removed under diminished pressure, the solution diluted to the original volume with water, and shaken with ether to remove the separated benzaldehyde. The aqueous layer, containing the glycerol ether, was neutralised and treated as already described, the yield of pure methylated glycerol obtained from 60 grams of the benzylidene compound being 22 grams. The constants of the glycerol methyl ether prepared by this method were determined for the purposes of comparison. B. p. 110—111°/13 mm., n_D 1·4461, D_4^{16} 1·1188, M_D 25·27. Calc., 25·36.

Reactions of Glycerol α-Methyl Ether.

The reactions of glycerol methyl ether are by no means simple. The compound is fairly readily oxidised, but the products are complex and difficult to separate, whilst, in addition, pronounced steric hindrance was encountered in attempts to substitute the hydroxyl groups by alkyl residues or by bromine. When heated with phthalic anhydride an amorphous product is obtained, consisting of a mixture of mono- and di-acid phthalates. Attempts to resolve these compounds were made, but were abandoned owing to the difficulty in separating the alkaloidal salts.

Condensation with Acetone.—For reasons explained in the introduction, the glycerol ether used in this experiment was obtained through the medium of benzylideneglycerol methyl ether. Twelve grams of glycerol methyl ether were dissolved in 90 c.c. of acetone containing 0·1 per cent. of hydrogen chloride, and the solution kept at the temperature of the room for forty-eight hours. Thereafter, the acid was removed with barium carbonate, followed by treatment with potassium carbonate, and the product isolated in the usual manner by fractionation under diminished pressure.

Found: C=57·60; H=9·62.

$C_4H_{10}O_3$ requires C=57·63; H=9·59 per cent.

B. p. 56°/14 mm.; n_D 1·4170; D_4^{17} 0·9888; M_D 37·13. Calc., 37·25.

Condensation with Benzaldehyde.—This reaction, which was conducted on glycerol methyl ether obtained from *iso*propylideneglycerol, gave considerable trouble on account of the ready hydro-

lysis of the product. Seven grams (1 mol.) of the methylated glycerol were dissolved in 14 grams (2 mols.) of benzaldehyde, which had been completely freed from benzoic acid by distillation at the Gaede pump. The flask was then attached to an upright condenser provided with a trap to retain the water formed in the condensation, and the mixture heated in an atmosphere of carbon dioxide. After eighty minutes at 150°, the temperature was maintained at 160° for an additional thirty minutes. On removal of the excess of benzaldehyde under greatly diminished pressure, a clear syrup remained, which boiled steadily at 120°/2 mm. Analysis showed the compound to be pure benzylideneglycerol methyl ether, giving the following constants:

n_D 1·5151; D_4^{17} 1·1253; M_D 52·00. Calc., 52·12.

Condensation with l-*Menthone.*—This reaction was carried out in a manner similar to that adopted in the preparation of *iso*propylideneglycerol. Fifty grams of the ketone ($[\alpha]_D$ −25°) were introduced into a gas absorption bulb, connected on one side to a trap containing standard alkali, and on the other to a graduated gasholder containing pure hydrogen chloride over mercury. The requisite volume of the gas necessary to make a 1 per cent. solution was then bubbled slowly into the ketone, the absorption being practically complete as indicated by titration of the contents of the trap. In the case of expensive ketones this method of preparing the standard acid solution is not only economical, but diminishes the risk of auto-condensation. The acid solution of *l*-menthone was diluted with an equal volume of ether, and then shaken for forty-eight hours with the methylated glycerol until a saturated solution was obtained. The subsequent neutralisation with silver carbonate proceeded very slowly, and was only complete on the addition of a small quantity of water. On working up the product in the usual manner the main fraction was collected between 125° and 140°/14 mm., and prolonged fractionation was necessary before a pure compound was obtained.

l-*Menthylideneglycerol methyl ether* is a colourless liquid (b. p. 135—136°/11 mm.), which could not be obtained crystalline.

Found: C = 69·00; H = 10·75.

$C_{14}H_{26}O_3$ requires C = 69·42; H = 10·74 per cent.

Solvent: 80 per cent. alcohol; c = 2·068; $[\alpha]_D^{20}$ −21·2°.

As the compound could not be obtained in a pure stereochemical form, an attempt was made to decompose it by fractional hydrolysis. A 2·7 per cent. solution of the compound in 60 per cent. alcohol, containing 0·2 per cent. of hydrogen chloride, was heated at 30° for seven hours, polarimetric readings being taken every ten minutes. Thereafter, observations were taken every hour for

one hundred and forty hours. During this treatment the lævorotation gradually diminished; after forty-three hours the solution was inactive, and the permanent value finally attained was $[\alpha]_D$ +9·3°. On plotting the optical values in a curve, no indication was obtained of the desired hydrolysis in stages, and it would appear that the results were obscured by the racemisation of the liberated ketone. In a parallel experiment, in which pure *l*-menthone, in the same concentration and in the same solvent, was heated for seventy-seven hours, the specific rotation altered from −19·1° to +12·1°.

Action of Phosphorus Tribromide.—To a solution of 30 grams of glycerol methyl ether in 150 c.c. of dry chloroform were added 50·5 grams of phosphorus tribromide dissolved in 250 c.c. of the same solvent. The mixture was cautiously heated, and finally boiled for forty-five minutes under a condenser. During this time hydrogen bromide was actively disengaged, and the solution became turbid. After remaining overnight, the clear liquid was decanted from the syrupy phosphorous acid, washed with sodium carbonate solution, then with water, and finally dried over potassium carbonate and distilled. Only 10 grams of distilled product were obtained (b. p. 49—50°/0·18 mm.), the bulk of the material, consisting of a clear acid syrup containing combined phosphorus, remaining undistilled, even when the bath was raised to 197°.*

On refractionating the distillate, it was evident that the product consisted of glycerol methyl ether bromohydrin (b. p. 76°/11 mm.) mixed with a small proportion of dibromomethoxypropane (b. p. 81°/17 mm.), which could not be removed by distillation. This idea was confirmed by analysis, and by the comparison of the physical constants given below (Found, Br=48·80. $C_4H_9O_2Br$ requires Br=47·34 per cent.):

	n_D.	*d*.	M_D.	M_D calc.
Glycerol methyl ether	1·4463	1·1197	25·26	25·36
Glycerol methyl ether bromohydrin	1·4820	1·5430	31·23	31·49
Dibromomethoxypropane	1·5143	1·8329	38·14	37·84

In order to complete the bromination, the bromohydrin, obtained as above, was treated in chloroform solution with one molecular proportion of phosphorus pentabromide similarly dissolved. The subsequent treatment was as usual, and the product on fractiona-

* The results of analyses and titrations show that this derivative has one of the following formulæ:

Found: P=13·18. $C_4H_{10}O_4BrP$ requires P=13·3 per cent.

tion (b. p. 80—81°/15 mm.) showed n_D 1·5055, and contained 63·9 per cent. of bromine. As the bromination was still incomplete, the total distilled material was subjected to further treatment with phosphorus pentabromide. This gave the desired product in a pure condition.

Found: Br = 68·60; n_D 1·5134; D_4^{12} 1·8337.

$C_4H_{10}OBr_2$ requires Br = 69·00 per cent.; n_D 1·5143; D_4^{20} 1·8329.

Action of Phosphorus Pentabromide.—With the object of preparing dibromomethoxypropane in one operation from glycerol methyl ether, 20 grams of the latter were treated in chloroform solution with 162·6 grams of phosphorus pentabromide, the subsequent processes being the same as described above. The result was disappointing, as only 3·2 grams of volatile material were obtained, whilst a considerable quantity of an acid syrup containing both phosphorus and bromine remained undistilled. The distillate, on fractionation, proved to be the desired dibromo-ether, a small quantity of a second product containing a larger proportion of bromine and showing a higher refractive index (n_D 1·5180) being also present.

Action of Ethyl Iodide and Silver Oxide.—Attempts to produce a mixed ether from glycerol α-methyl ether by means of the silver oxide reaction resulted in simultaneous alkylation and oxidation. In the first ethylation, in which twice the theoretical proportion of the alkylating mixture was employed, ether was used as a solvent, but the indefinite boiling point of the product (50—60°/9 mm.) showed that a mixture of compounds had resulted. After a second alkylation, in which no extraneous solvent was necessary, the main product gave, on fractionation, *ethyl β-methoxy-α-ethoxypropionate* as a colourless, mobile liquid (b. p. 57—58°/12 mm.).

Found: C = 54·64; H = 10·03.

$C_8H_{16}O_4$ requires C = 54·55; H = 9·99 per cent.

Conversion of Glycerol α-Methyl Ether into βγ-Dibromo-α-methoxypropane.

Twenty grams of the alkylated glycerol were mixed with 8 grams of anhydrous oxalic acid and a trace of ammonium sulphate, and the mixture was heated at 180° for two hours. Thereafter, the temperature was raised to 230° for eight hours, and, from time to time, additional quantities of oxalic acid amounting to 20 grams were added. Throughout the decomposition, the flask was fitted to an upright condenser furnished with a trap for the retention of volatile products, which were thus prevented from returning to the reaction mixture.

The colourless distillate thus obtained consisted of nearly pure methyl allyl ether, but later fractions contained quantities of what appeared to be formic acid. The united distillates were dissolved in chloroform and kept in contact with anhydrous potassium carbonate until neutral. Bromine, dissolved in chloroform, was then added until saturation had been effected, the solution washed with potassium carbonate solution, and then with water, dried over magnesium sulphate and distilled. On removal of the solvent, the residual oil was fractionated under diminished pressure, and an excellent yield of βγ-dibromo-α-methoxypropane was thus obtained:

B. p. 83—84°/17 mm.; n_D 1·5141; D_4^{12} 1·8320; M_D 38·17 (calc., 37·84).

Synthesis of Glycerol α-Methyl Ether.

The substitution of hydroxyl for bromine in dibromomethoxypropane does not proceed readily, and the removal of the halogen by powerful reagents results in the regeneration of unsaturated compounds. Heating with moist silver oxide led to oxidation, whilst heating in a sealed tube with potassium carbonate solution, barium hydroxide solution, or with pure water gave no satisfactory result. On boiling an aqueous-alcoholic solution of the bromo-compound with silver acetate for several hours very little reaction took place, and the mixture was accordingly transferred to a sealed tube and heated at 160° for thirty hours. The liquid thus obtained was filtered from silver bromide and dried over anhydrous potassium carbonate, after which the alcohol was removed. The semi-solid residue was dissolved in acetone, filtered from potassium acetate, and the product isolated by distillation, but the indefinite boiling point (95—105°/12 mm.) and the results of analyses showed that the diacetate had been partly hydrolysed.

The total product was accordingly boiled for thirty minutes with 5 per cent. aqueous barium hydroxide, the barium afterwards being precipitated as carbonate, and the methylated glycerol isolated by distillation (b. p. 109—110°/10 mm.).

Found: C = 45·32; H = 9·45.

$C_4H_{10}O_3$ requires C = 45·28; H = 9·43 per cent.

Preparation of Methyl Allyl Ether and of βγ-Dibromo-α-methoxypropane.

The above compounds were prepared in a specially pure condition so that their physical constants might be determined for the purposes of comparison.

Methyl Allyl Ether.—Two methods of preparation were em-

ployed, namely, (*a*) methylation of allyl alcohol by the silver oxide reaction, and (*b*) decomposition of allyl iodide by means of sodium methoxide. No experimental details need be given, as both processes were conducted on standard lines, and identical results were obtained in each case. By the decomposition of 160 grams of allyl iodide and repeated distillation of the product over a long fractionating column, 65 grams of pure methyl allyl ether were obtained. The following constants were determined:

B. p. 42·5—43°/757 mm.; n_D varied from 1·3778 to 1·3803.

βγ-Dibromo-α-methoxypropane.—Fifty-six grams of pure methyl allyl ether were brominated in the usual manner, and the product was fractionated repeatedly until a constant refractive index was observed. In this way 122 grams of the dibromide were obtained, showing the following constants:

B. p. 81°/16 mm.; D_4^{20} 1·8329; n_D 1·5143; M_D 38·14 (calc., 37·84).

We are indebted to the Carnegie Trust for a research grant in aid of the above investigation, and to Miss Winifred Ross for much valuable assistance.

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XL.—*The Molecular Complexity of Acetic Acid.*

By GEORGE MACDONALD BENNETT.

WHILST the problem of the degree of association of acetic acid in the liquid state has been examined in the past by means of all the well-recognised physical methods, the surface tension data required for the calculation of surface energy are disconnected and incomplete. Ramsay and Shields' determinations (*Phil. Trans.*, 1893, [*A*], **184**, 647) did not extend to temperatures below 130°; other determinations have recently been made by various methods (Morgan, *J. Amer. Chem. Soc.*, 1911, **33**, 640; Worley, T., 1914, **105**, 278), but only three values were obtained by each of these workers. A re-determination of the surface tension of acetic acid between 15° and 150° has therefore been made.

EXPERIMENTAL.

Apparatus and Method.—The method adopted was that depending on the measurement of capillary rise in the absence of air.

The apparatus was a modification of that used by Hewitt and Winmill (T., 1907, **91**, 441), which latter was designed for use with non-volatile substances, and has considerable disadvantages when used with volatile liquids. Moreover, the examination, with that apparatus, of a liquid above its boiling point was out of the question. The tube actually used is shown in Fig. 1. It was exhausted and sealed after introduction of the liquid, and the whole tube was then immersed in the bath. The essential wetting of the capillary wall was ensured by tilting the tube. The bath consisted of a large beaker containing $1\frac{1}{2}$ litres of water or glycerol, stirred mechanically, and it was found possible to adjust the temperature accurately for considerable periods. The thermometers were graduated to 0·2°, and were compared with one another and with a certified thermometer. Observations of the difference of the levels of the liquid in the capillary and in the larger limb were made with a cathetometer at intervals of 5° from 15° to 150°, the mean of five or six concordant readings being adopted for each temperature.

FIG. 1.

The capillary tube itself was one selected with care having a bore which did not vary by more than one part in 2000, as found by measuring the lengths of several mercury threads by means of a dividing machine. The radius r was determined accurately by weighing mercury threads, the value obtained being subsequently confirmed after the capillary had been built into the apparatus, by observing the capillary rise of pure benzene; by weighing of mercury r was found = 0·02407 cm. The mean value calculated from the observed capillary rise and that found by Ramsay and Aston (*Zeitsch. physikal. Chem.*, 1894, **15**, 89) was $r = 0{\cdot}02403$ cm.*

The values of surface tension were calculated from the formula:

$$= \tfrac{1}{2}g(h + r/3)r(d - d'),$$

where h = capillary height, d the density of the liquid, and d' that of the vapour, the latter factor becoming of importance at higher temperatures The values of d and d' were taken from the work

* The values of r found were: at 14·4°, 0·02384 cm.; at 39·9°, 0·02394 cm.; at 74·6°, 0·02432 cm.; mean 0·2403 cm. The values of service tension here appear to have a different temperature slope from that found by Ramsay and Aston. Mr. A. D. Mitchell has pointed out to the author that Walden and Swinne and also Mitchell and Smith (see below) found a similar discrepancy in the same direction. The values obtained by Ramsay and Aston would therefore appear to be at fault.

of Ramsay and Young (T., 1886, **49**, 806); the values of d given by these workers agree closely with those obtained from the latest density determinations and the expansion formula of Zander (*Annalen*, 1884, **224**, 61). The slight correction for the capillary rise in the larger tube was calculated from the formula given by Walden and Swinne (*Zeitsch. physikal. Chem.*, 1912, **79**, 705).

Table I.

Surface Tension of Acetic Acid.

T.	h from curve, cm.	$h+r/3$ corrected, cm.	d.	d'.	$d-d'$.	γ dynes per cm.
10°	2·304	2·315	1·0593	—	1·0593	28·96
20	2·242	2·252	1·0491	0·0001	1·0490	27·90
30	2·180	2·190	1·0392	0·0001	1·0391	26·87
40	2·118	2·128	1·0284	0·0002	1·0282	25·84
50	2·056	2·066	1·0175	0·0003	1·0172	24·82
60	1·994	2·004	1·0060	0·0005	1·0055	23·80
70	1·932	1·942	0·9948	0·0007	0·9941	22·80
80	1·869	1·878	0·9835	0·0009	0·9826	21·79
90	1·807	1·816	0·9718	0·0013	0·9705	20·81
100	1·745	1·754	0·9599	0·0018	0·9581	19·84
110	1·683	1·692	0·9483	0·0025	0·9458	18·90
120	1·621	1·630	0·9362	0·0033	0·9329	17·96
130	1·557	1·566	0·9235	0·0043	0·9192	17·00
140	1·495	1·504	0·9108	0·0055	0·9053	16·08
150	1·433	1·442	0·8978	0·0067	0·8911	15·17

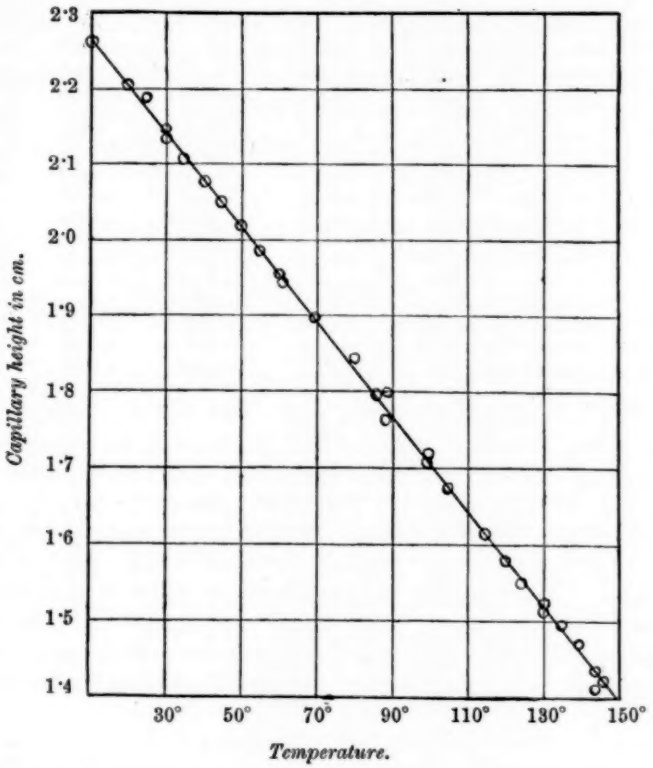
Material.—Commercial glacial acetic acid was fractionally frozen a few times, and then purified by the method recommended by Bousfield and Lowry (T., 1911, **99**, 1440). The acid used was from a fraction of more than 100 grams of constant boiling point. It was again purified by freezing. The tube was thoroughly cleaned, washed successively with fuming nitric acid and distilled water, and dried. After the tube had been rinsed out with the pure acid a considerable quantity of the latter was introduced and partly frozen in the tube. The still liquid portion was poured off, and the tube immediately exhausted (the liquid being now warmed) and sealed.

Results.—When the observed heights were plotted against temperatures, the curve was found to be a straight line (Fig. 2). Smoothed heights were taken from this curve for the calculation of the surface tensions given in table I.

Other determinations of the surface tension of acetic acid which have been made are as follows: Ramsay and Shields and Worley using the method of capillary rise; Morgan by the drop-weight method; and Jaeger and Smit by observations of the pressure required to produce bubbles of pure nitrogen beneath the liquid (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 329), the last

having been published while the present work was in progress. In table II the values obtained by all the observers are compared (some of these values were found by interpolation). The agreement between the results of the present investigation and those of Morgan and of Jaeger and Smit is very fair, in view of the fact that three entirely distinct methods were used. It is stated by Bousfield and Lowry that the removal from acetic acid of the last traces of impurities, other than water, is impossible by fractional

FIG. 2.



freezing alone, but that it is at once accomplished by their method of distillation from solid potassium permanganate. It seems probable, therefore, that the material used in the present case was purer than that used by other observers. The higher homologues and other compounds present as impurities, being hydroxylic, would tend to cause dissociation, and so to lower the surface tension. The divergence of the values given by Ramsay and Shields and by Worley from the others in table II can be explained only in this

way. The material used by Ramsay and Shields was purified by repeated freezing; that of Morgan "by the methods recommended by previous workers on surface tension"; Worley's acid "distilled between 117·5° and 118°"; and Jaeger and Smit's material was purified by repeated freezing and distillation. A specimen of the commercial frozen acid, which had not been further purified, was

TABLE II.

Comparison of Values of Surface Tension obtained by Various Observers.

Temperature.	Ramsay and Shields.	Morgan.	Jaeger and Smit.	Bennett.	Worley.
20°	—	27·43	27·6	27·90	26·670
50	—	24·53	24·5	24·82	23·809
70	—	22·65	22·4	22·80	21·808
118·1	—	—	17·7	18·14	—
130	16·18	—	—	17·00	—
150	14·46	—	—	15·17	—

examined for comparison (without exhaustion and sealing of the tube), and at 15·5° the commercial acid gave $h=2·226$ cm.; the pure acid (under the same conditions) gave $h=2·264$ cm. The difference of nearly 2 per cent. supports the above considerations.

Interpretation of Results.

It should by now be generally admitted that the criterion of non-association in liquids is not the absolute value of $k=\frac{d[\gamma(Mv)^{\frac{1}{3}}]}{dt}$, but rather its constancy for the given liquid. The value 2·121, which was the mean of the figures for the six normal liquids examined by Ramsay and Shields, is evidently of no general significance, since a large number of liquids have been found by Dutoit (*J. Chim. phys.*, 1903, **1**, 358; *Arch. Sci. phys. nat.*, 1900, [iv], **9**, 105); Guye (*J. Chim. phys.*, 1903, **1**, 505; *Arch. Sci. phys. nat.*, 1901, [iv], **11**, 449, 537); Walden (*Zeitsch. physikal. Chem.*, 1910, **75**, 555), and others, which, being mostly esters or hydrocarbons, are of the most typically normal unassociated type (and were further in several cases tested by molecular-weight determinations by the cryoscopic method), and nevertheless gave very abnormal values of k.

Values greater than 2·12 form a continuous series, the highest yet observed being 6·21 (Walden, *loc. cit.*); but a few cases have been found where k is less than 2·12, although the liquids are

certainly not associated, since both k and the total molecular surface energy K (see below) are constant; for example:

	k.	
Liquid oxygen.....	1·92	(Baly and Donnan, T., 1902, **81**, 907).
Diethyl sulphite	1·95	(Walden, *loc. cit.*).
Liquid hydrogen.....	1·46	(Kamerlingh Onnes and H. A. Kuypers, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528).

Further it has been repeatedly found (Walden and Swinne, *Zeitsch. physikal. Chem.*, 1912, **79**, 755; Guye, *loc. cit.*; and Mitchell and Smith, T., 1913, **103**, 489) that the value of k for normal liquids tends to fall slightly with rise of temperature. This, in fact, seems to be the rule rather than the exception. We must therefore conclude that k, which Ramsay considered a constant for all normal liquids at all temperatures, has widely divergent values for various normal liquids, and that the values with any one liquid have a uniform tendency to fall as the temperature is raised.

On the other hand, it was shown by Bennett and Mitchell (*Zeitsch. physikal. Chem.*, 1913, **84**, 475) that almost without exception liquids previously recognised as normal have a total molecular surface energy, $\left(\gamma - t\,\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}}$, which is quite constant up to temperatures near the critical point. This function is most fundamental from the theoretical point of view, since the total surface energy is at once deducible from the free surface energy (numerically equal to surface tension) γ by means of the Helmholtz equation:

$$A - U = t\,\frac{dA}{dt}.$$

The constancy of the function $\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}} = K$ is therefore a much better criterion of normality or an unchanged degree of association in any liquid. With substances known to be associated, such as water and the lower alcohols, values of K were found which rose rapidly and continuously with increase of temperature, and the assumption was here made (analogous to that made by Ramsay and Shields) that if the corrected molecular weight Mx (where x = degree of association) could have been used in place of M for the calculation of the values of total molecular surface energy for these liquids, the results would have given a constant as with normal liquids. Hence to find x we require the theoretical value of K, which would be obtained in this manner. The calculation of K from atomic values will probably be possible for all compounds when further and more consistent data are available.

To turn now to the values obtained in the present work, the

same conclusions can be deduced whether we adopt the more recent methods of handling k or the function $\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}}$. In table III these values are tabulated. It is seen that k varies from 1·275 at 25° to 1·265 at 85° and 1·250 at 145°; the value is therefore nearly constant with the usual slight fall as the temperature is raised. Acetic acid behaves as an unassociated liquid, or as one having a constant degree of association. The total molecular surface energy K, on the other hand, remains sensibly constant over the entire range studied, varying from 871 to 883 ergs with a mean of 877. In view of the method of calculation (in which the inevitably large errors in $\frac{d\gamma}{dt}$ are multiplied by the absolute temperature) the diverg-

TABLE III.

Free and Total Molecular Surface Energies of Acetic Acid.

t. absolute.	γ.	$-\frac{d\gamma}{dt}$.	$-t\frac{d\gamma}{dt}$.	$\gamma - t\frac{d\gamma}{dt}$.	$\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}} = K$ ergs.	$\gamma(Mv)^{\frac{2}{3}}$. ergs.	k.
288	28·42	0·106	30·53	59·95	872	420·7	—
298	27·38	0·104$_5$	31·14	58·52	872	407·8	1·275
308	26·35	0·103$_5$	31·72	58·07	871	395·2	1·270
318	25·32	0·102	32·44	57·76	872	382·4	1·270
328	24·30	0·101	33·13	57·43	872	369·8	1·270
338	23·29	0·100	33·80	57·09	875	357·0	1·275
348	22·30	0·099	34·45	56·75	876	344·3	1·265
358	21·30	0·098	35·08	56·38	877	331·5	1·250
368	20·33	0·097	35·70	56·03	879	319·0	1·250
378	19·37	0·096	36·29	55·66	881	306·5	1·250
388	18·43	0·095	36·86	55·29	883	294·0	1·260
398	17·48	0·094	37·41	54·89	883	281·3	1·270
408	16·54	0·092$_5$	37·74	54·08	881	268·6	1·260
418	15·62	0·091$_5$	38·04	53·66	880	256·1	1·250
428	14·72	0·090	38·52	53·24	881	243·6	—

ence of the value of K from their mean is not excessive, and no general tendency for K to rise or fall continuously with increase of temperature is indicated. Here again and still more convincingly, we have proof that acetic acid is behaving as a normal liquid between the temperatures 15° and 150°.

There are therefore two possibilities, namely:

(a) that a molecule, $(C_2H_4O_2)_n$ (where n may be 1, 2, 3, etc.), is behaving as a stable simple molecule, and that the liquid consists exclusively of such molecules, and

(b) that in the liquid there is a state of equilibrium such as:

$$(C_2H_4O_2)_2 \rightleftharpoons 2C_2H_4O_2,$$

which is, however, unchanged by alterations of temperature. The bath was kept at 140° on one occasion for three hours without the detection of any change in the capillary rise; there can be no doubt,

therefore, that a steady state had been reached. If temperature has no influence, the dissociation of the double into two simple molecules must involve no thermal effect. The latter alternative (*b*) cannot, however, be correct, since it is well known that acetic acid in the state of vapour becomes completely dissociated, by raising the temperature to 180°, from which it follows that the equation:

$$(C_2H_4O_2)_2 = 2C_2H_4O_2$$

does not represent a change unaffected by temperature. The inevitable conclusion is, therefore, that an unaltered molecule, $(C_2H_4O_2)_2$, persists throughout. The value of n is undoubtedly 2, since the vapour at the boiling point has a composition approaching $(C_2H_4O_2)_2$, and in solution in non-hydroxylic solvents acetic acid shows a doubled molecular weight. Acetic acid is therefore a normal liquid consisting exclusively of the complex molecules $(C_2H_4O_2)_2$. The experiments of Baud (*Bull. Soc. Chim.*, 1913, [iv], **13**, 435), which appeared just after this work had been undertaken, lead him to a similar conclusion. By a cryoscopic method of his own device he finds that acetic acid has the doubled molecular weight when dissolved in any concentration in the non-hydroxylic solvents ethylene dibromide, benzene, toluene, naphthalene, nitrobenzene, and chlorobenzene. He draws the conclusion that the term "association" is out of place in connexion with acetic acid, since it is a pure bimolecular liquid. The evidence adduced by Baud would support this view only at certain temperatures below 80°, whereas the conclusions deduced from the results of the present investigation are applicable to the whole range of temperature from 15° to 150°.

It is interesting to note that Eötvös in his classical work on surface energies (*Ann. Phys. Chem.*, 1886, [iii], **27**, 459) examined acetic acid and found values of k, between 21° and 160°, which were constant and $=1{\cdot}29$, from which he concluded that, since by using a doubled molecular weight this became 2·07, the molecule of acetic acid was a doubled one over this range of temperature. This is in accordance with the author's results, but not with those of Ramsay and Shields' (*loc. cit.*).

As regards other evidence as to the degree of association of acetic acid, a large number of expressions have been devised which should be applicable in the present instance, but the majority of them may be relied on merely as tests of association, and do not lead to trustworthy values of the degree of association. The results of the application of a few of these tests to the present problem may, however, be mentioned briefly.

Since the values of k found by the author are nearly constant

the correction devised by Ramsay (*Zeitsch. physikal. Chem.*, 1894, **15**, 112) for his original expression $x=\left(\frac{2\cdot121}{k}\right)^{\frac{2}{3}}$ is not required and we should have $x=\left(\frac{2\cdot12}{1\cdot27}\right)^{\frac{2}{3}}=2\cdot16$, but this value is, of course, quite crude, since the figure 2·12 has now been discredited.

Several other expressions refer to a value of x at the boiling point. Longinescu's $\left(\frac{T'}{100d}\right)^2=n$ (*J. Chim. phys.*, 1903, **1**, 296) gives $x=2\cdot17$; Walden's capillarity formula, $x=\frac{1\cdot16\times T}{Ma^2}$, gives $x=1\cdot92$ (*Zeitsch. physikal. Chem.*, 1908, **65**, 129), Traube's molecular volume method gives $x=1\cdot56$ (*Ber.*, 1897, **30**, 275). Nernst found his modified Trouton's rule was obeyed by acetic acid if $x=1\cdot65$. Lastly, we have to take into consideration the fact that the vapour at the boiling point has a composition represented by a value of $x=1\cdot68$ (Ramsay and Young, *loc. cit.*), which makes it probable that for the liquid $x>1\cdot68$. One other point may be mentioned as of some significance; it has been pointed out recently (Dunstan and Thole, "The Viscosity of Liquids," p. 5) that the variation of the viscosity of acetic acid with temperature resembles that shown by normal liquids rather than that of other associated liquids, such as formic acid.

Taking into consideration all the evidence cited, the conclusion arrived at above by the author does not appear to be affected; it would seem, rather, that we have here an interesting case in which we may test the accuracy of the various methods that have been proposed to determine the degree of association of liquids.

The conclusion that acetic acid exists as a pure bimolecular liquid even up to a temperature of 150° is a striking one. The union of the two simpler molecules must be of a relatively stable character, yet it vanishes the moment the acid is dissolved in water. The complex acid should be dibasic, and give rise to a series of acid salts. These are the well known binacetates, $MC_2H_3O_2,C_2T_4O_2$, where M may be Li, Na, K, NH_4,Tl. These salts are anhydrous, and show considerable stability; for instance, potassium binacetate melts at 148°, and only at 200° is the extra molecule of acetic acid driven off. It is possible that a normal acetate would prove to be bimolecular in solution in a non-hydroxylic solvent.

The homologues of acetic acid appear not to have been much investigated, but it should be mentioned that the values of K calculated (Bennett and Mitchell, *loc. cit.*) from the determination of surface tension of Ramsay and Shields (T., 1893, **63**, 1089) for five members of this series of aliphatic acids were fairly con-

stant over considerable ranges of temperature. This seems to indicate that these homologues are in a similar condition in the liquid state to that now established for acetic acid itself.

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XLI.—*The Organic Phosphoric Acid of Wheat. (Preliminary Note.)*

By GEORGE CLARKE.

FINELY ground wheat was extracted with 0·2 per cent. hydrochloric acid, and the pale brown extract treated as described in preparing phytin, $C_{12}H_{22}O_{44}P_{10}Ca_7Mg$, from mustard (T., 1914, **105**, 535). A white, amorphous substance was obtained resembling the latter substance in chemical and physical properties. The yield was 0·14 per cent. of air-dried wheat.

The substance thus obtained was a mixture of complex calcium and magnesium salts of the type $C_{12}H_{22}O_{44}P_{10}Ca_7Mg$, but differing slightly in their solubility in boiling dilute acetic acid.

The two successive fractions most sparingly soluble in boiling dilute acetic acid gave the following results as the mean of several closely agreeing determinations:

I. C = 9·08, H = 1·51, P = 21·45, Ca = 14·67, Mg = 4·64.
II. C = 9·17, H = 1·54, P = 20·98, Ca = 15·21, Mg = 4·18.

When heated under pressure at 130° with 30 per cent. sulphuric acid this substance was decomposed into inositol [hexa-acetylinositol, m. p. 211—212° (uncorr.)] and phosphoric acid. Ten grams of air-dried, corresponding with approximately 8 grams of anhydrous, substance yielded 1·5 grams of inositol.

The calcium magnesium salt obtained from wheat differed in composition from that extracted from mustard, and separated by similar methods (*loc. cit.*). The free acid obtained from the calcium magnesium salt described above by preparing the lead salt, and decomposing the latter with hydrogen sulphide, consisted of a mixture of an organic phosphoric acid and phosphoric acid. The strychnine salt of the former acid is sparingly soluble in water, from which it crystallises in slender needles melting at 218—219° (uncorr.). The strychnine salt of the inositolphosphoric acid obtained from phytin extracted from mustard, and prepared and purified by similar methods, melted at 203—204° (uncorr.).

THE CHEMICAL LABORATORY,
UNITED PROVINCES, DEPARTMENT OF AGRICULTURE,
INDIA. [*Received, Feb. 4th*, 1915.]

XLII.—*The Estimation of Potassium by the Perchlorate Method.*

By Russell Gibson Thin and Alexander Charles Cumming.

The determination of potassium as perchlorate was proposed as early as 1831 by Sérullas (*Ann. Chim. Phys.*, 1831, [ii], **46**, 294), and the method has been examined and recommended by many others (F. Hamel, *Chem. News*, 1892, **26**, 27; Kreider, *Chem. News*, 1895, **72**, 241; 1896, **73**, 8; Kreider and Breckenbridge, *Zeit. anorg. Chemie*, 1897, **13**, 161; Shiver, *Chem. News*, 1899, **79**, 269). In spite of these investigations, the method has never been generally adopted in this country, and was therefore critically re-examined by W. A. Davis (*J. Agric. Science*, 1912, **5**, 52). He strongly recommended the perchlorate method, and regards it as superior to the platinichloride method.

Our attention was specially directed to the method in a somewhat curious manner. It was found that the analysis of pure potassium chloride, following Davis's procedure as detailed on p. 57 of his paper, gave slightly high results, although, from the amount of wash-liquor used, the results should have been at least a milligram low. An examination of Davis's figures showed that individual results often diverged far more from the correct result than should be the case with an accurate quantitative method. Davis, in discussing his results, suggests that the errors often met with were due to the solubility of the precipitate in the washing solution, 95 per cent. alcohol containing 0·2 per cent. of perchloric acid. He suggests and describes the use of 95 per cent. alcohol, saturated with potassium perchlorate, as washing solution, although this was not used for the analyses which he quotes. Our difficulty was to explain the high results. In the literature generally, there seems to be a tendency to regard the perchlorate method as giving only approximately correct results; for example, the writer of the analytical section of the Annual Reports for 1912 refers to "the perchlorate method, which admittedly falls short of exactness." Some of the earlier investigators, on the other hand, recommend the method as exact. In view of this divergence of opinion as to the accuracy of the method, further examination appeared desirable. Our investigation falls roughly into two parts; first, the determination of the solubility of potassium perchlorate in various solvents, and, secondly, the trial of the procedure for analysis suggested by the solubility determinations.

Experimental.

Cause of High Results.—The explanation of the high results we obtained in determining potassium by this method was discovered at an early stage of the investigation. The perchloric acid used was Merck's "pure" 20 per cent. perchloric acid. Ten c.c. of one sample of this acid gave on evaporation to dryness 0·1476 gram of a solid residue, which was found to consist of sodium chloride and perchlorate with a trace of potassium salt. Another 10 c.c. sample, from a bottle bought a year later, gave 0·0492 gram of a similar solid residue. Perchloric acid containing some sodium perchlorate can be prepared more cheaply than pure perchloric acid (F. C. Mathers, *J. Amer. Chem. Soc.*, 1910, **32**, 66), and, provided that only the sodium salt is present, the accuracy of the method is not affected by the use of this acid. In Merck's perchloric acid, however, there was not only an unnecessarily high percentage of sodium perchlorate, but there was also a trace of potassium salt.

We prepared a quantity of perchloric acid from ammonium perchlorate (Willard, *J. Amer. Chem. Soc.*, 1912, **34**, 1480), but found that it contained nitric acid, and was therefore useless for our purpose, though quite good for ordinary analytical work. For all experiments detailed below, the acid used was purified by redistillation under reduced pressure.

Solubility Determinations.

Solubility of Potassium Perchlorate in Water.—The solubility of potassium perchlorate in water has been determined by M. M. P. Muir (*Chem. News*, 1876, **33**, 15):

Temperature	0°	25°	50°	100°
Grams per 100 grams of solution	0·705	1·92	5·07	15·76

and also by Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 530), who obtained the following values:

Temperature.....	10°	20°	30°
Grams per litre	10·82	16·68	24·94

The results of our solubility determinations are given in the following table:

Solubility of Potassium Perchlorate in Water.

Temperature.	Vol. of solution (c.c.)	Weight of solution (grams).	Weight of $KClO_4$ obtained.	Grams $KClO_4$ per 100 grams of water.	Grams $KClO_4$ per litre of solution.
11·4	100	100·45	1·1558	1·567	11·56
	100	100·45	1·1551		
25·2	25	25·24	0·5259	2·085	21·04
	25	25·24	0·5249		
	25	25·24	0·5273		

In the determination of potassium by the perchlorate method, as ordinarily carried out, other perchlorates are extracted with alcohol, and the potassium perchlorate finally washed with a 0·2 per cent. solution of perchloric acid in alcohol. The solubility of potassium perchlorate in aqueous perchloric acid solutions and aqueous alcohol solutions was therefore determined. The experimental temperature was higher than would be usual in analytical practice, but the higher temperature has the advantage that it increases all values and makes the differences more marked.

Solubility of Potassium Perchlorate in Aqueous Perchloric Acid at 25·2°.

Concentration of $HClO_4$ N.	Weight of solution taken (grams).	Weight of $KClO_4$ obtained (grams).	Grams $KClO_4$ per 100 grams of solution.	
(Water)	—	—	—	2·085
0·01	25·18	0·5054	2·006	1·999
	25·19	0·5018	1·992	
0·1	25·24	0·3749	1·486	1·485
	25·23	0·3740	1·483	
1·0	26·33	0·1385	0·5260	0·527
	26·32	0·1391	0·5284	

Solubility of Potassium Perchlorate in Alcohol at 25·2°.

Per cent. alcohol. (By volume.)	Weight of solution taken (grams).	Weight of $KClO_4$ obtained.	Solubility grams per 100 grams of solution.
(Water)	—	—	2·085
51·2 (sp. gr. 0·9319)	23·13	0·1741	0·754
	22·60	0·1707	
93·5 (sp. gr. 0·8219)	20·29	0·0104	0·051
	20·28	0·0103	
98·8 (sp. gr. 0·7998)	35·96	0·0073	0·019
	41·07	0·0076	

It is evident from the above figures that the amount of water in the alcohol used will have a very large effect on the amount of potassium perchlorate dissolved.

Experiments were next carried out to find how much the solubility was reduced by addition of perchloric acid. The solvents used were prepared by addition of 20 per cent. aqueous perchloric acid to alcohol of known concentration.

Solubility of Potassium Perchlorate in Alcohol–Perchloric Acid Solutions at 25·2°.

Solvent.	Weight of solution taken (grams)	Weight of $KClO_4$ obtained.	Solubility grams per 100 grams solution.
93·5 per cent. alcohol	—	—	0·051
93·5 per cent. alcohol with ...	31·53	0·0035	0·0176
0·2 per cent. perchloric acid	31·59	0·0035	
98·8 per cent. alcohol	—	—	0·019
98·8 per cent. alcohol with 0·2 per cent. perchloric acid	31·04		
	29·84	0·0019	0·010
		0·0019	
98·8 per cent. alcohol with 2 per cent. perchloric acid.	32·93	0·0060	0·028
	31·66	0·0054	

In these experiments, the diminution in solubility produced by addition of perchloric acid is more or less counterbalanced by the increase of solubility caused by the water added with the perchloric acid. The solubility in 0·2 per cent. perchloric acid (10 c.c. of 20 per cent. perchloric acid made up to 1 litre with 98·8 per cent. alcohol) is about one-half the solubility in 98·8 per cent. alcohol, but with further addition of 20 per cent. perchloric acid the solubility greatly increases.

Solubilities of other Perchlorates.—One of the special advantages of the perchlorate method is that all perchlorates except those of potassium and ammonium are readily soluble, and that it is unnecessary completely to remove other metals prior to the determination of potassium. The perchlorates of lithium, magnesium, and barium were prepared with the intention of comparing their solubilities in alcohol with that of potassium perchlorate. The perchlorate was found in each case to be so readily soluble, even in absolute alcohol, that quantitative determinations were regarded as unnecessary for our purpose. Ammonium perchlorate is sparingly soluble in water, and some determinations of its solubility in various solvents were therefore tried. It was prepared from ammonia and perchloric acid, and recrystallised from water.

Solubilities of Ammonium Perchlorate.

Temp.	Solvent.	Weight of sol. taken (grams).	NH_4ClO_4 present.	Solubility grams per 100 grams.
14·2°	Water	80·26 (100 c.c.)	1·361	1·735
25·2°	Absolute alcohol ... (98·8 per cent).	29·07	0·5728	1·971
		19·55	0·3829	1·958
25·2°	0·2 per cent. perchloric acid in 98·8 per cent. alcohol.	19·99	0·396	1·98
		19·97	0·394	1·97

The solubility of ammonium perchlorate in alcohol solutions is small enough to suggest the probability of error if potassium is determined in presence of any considerable quantity of ammonium salt.

Experiments on the Washing of Precipitates.—The minimum solubility of potassium perchlorate in the various solvents tried is in 98·8 per cent. alcohol containing 0·2 per cent. of perchloric acid. Even in this solvent the solubility is 10 mg. per 100 grams of solution, and is therefore far too high for satisfactory results to be expected when this is used as the washing solution. There is some difficulty in deciding what error would be introduced in practice. We found that in general practice, with Gooch crucibles, the volume of wash-liquor we used was always between 30 and 60 c.c. Another analyst used as much as 150 c.c. for washing, and Davis (*loc. cit.*) mentions the use of 20 to 150 c.c. of washing solution. Some experiments were tried to ascertain the probable error caused by washing with various solvents. A perchlorate determination with a pure potassium salt was carried out, and the precipitate washed until undoubtedly free from any adhering matter. The residue was dried, and weighed in a Gooch crucible. It was then washed with six portions of the wash-liquor, using, as a rule, about 30 c.c. of liquid, and again dried and weighed. As an example, some data regarding the washing of potassium perchlorate with 98·8 per cent. alcohol may be quoted:

Original weight of precipitate = 0·3745. Six washings in each case Temperature of alcohol from 20° to 22°.

Volume used (c.c.).....	=	32	36	30	34
Loss in weight (milligrams)	=	1·7	1·6	1·2	1·7

Similar sets of experiments were performed with various washing solutions, and a comparison of the results is of interest. In all cases, the washing solution was at room temperature:

(1) With absolute (98·8 per cent.) alcohol, loss was 4·7 mg. per 100 c.c. of washing solution.

(2) With absolute alcohol containing 0·2 per cent. of perchloric acid, the loss was 1·3 mg. per 100 c.c. of washing solution.

These experiments show clearly the error caused by the solubility of the precipitate, and prove that neither of these solutions is satisfactory as a washing solution for this determination. Davis has recommended and used a saturated solution of potassium perchlorate in alcohol as a washing solution. Solutions were made by shaking potassium perchlorate with (1) absolute alcohol and (2) rectified spirit (94 per cent. alcohol). Washing with these solutions was found to produce no change in weight beyond one- or two-tenths of a milligram up or down. One point only requires

special attention in connexion with the use of this washing solution. It is most conveniently prepared by shaking some crystals of potassium perchlorate with alcohol at room temperature for about ten minutes, and pouring off the solution as soon as the crystals have settled. The solution must be shaken with potassium perchlorate shortly before use. If an old solution is used, the results are often high or low, through the solution becoming supersaturated or unsaturated on account of a change in temperature.

Application to Quantitative Practice.—Experiments on the determination of potassium in various solutions proved that:

(1) Ammonium salts must not be present in quantity.

(2) The evaporation with perchloric acid must be carried far enough to ensure complete conversion of chlorides into perchlorates.

(3) Other salts, even up to 2 grams of various chlorides, have no effect.

(4) A freshly prepared solution of potassium perchlorate in alcohol is the only satisfactory solution for washing the precipitate.

If these conditions were complied with, the error did not exceed 0·5 mg. on the weight of the potassium perchlorate, and was often less. Our final procedure was therefore practically identical with that recommended by W. A. Davis, and we find that the method is accurately quantitative under these conditions. All the analyses quoted in Davis's paper were carried out using 95—96 per cent. alcohol containing 0·2 per cent. of perchloric acid for the main portion of the washing. This probably explains the variations in his values. Our experience confirms the statement at the conclusion of his paper, that a high degree of accuracy is attainable if alcohol saturated with perchlorate is used as washing solution. Our results show that the method is not accurately quantitative if any other washing solution is used, and we desire also to direct attention to the error which may be introduced if commercial "pure" perchloric acid or perchlorates are used.

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[*Received Feb. 17th*, 1915].

XLIII.—*The Removal of Oxygen from Triethylphosphine Oxide.*

By John Norman Collie and Frank Reynolds.

Amongst the organic compounds the oxides of the tertiary phosphines are substances of some interest. Unlike the usual compounds of phosphorus with oxygen, they form salts with acids and not with bases. Moreover, they are compounds of the most extraordinary stability; triethylphosphine oxide may be boiled with any oxidising reagents, and it remains unchanged, and Hofmann, its discoverer, mentions that it can be "distilled from sodium without experiencing the slightest alteration." It also is impossible to determine the phosphorus in it by heating it in a sealed tube with nitric acid; in fact, in Hofmann's papers on the phosphorus bases (*Phil. Trans.*, 1860, **147**, 575) he never mentions a single phosphorus determination of any of the compounds he prepared. Ordinary reducing agents leave it unchanged. The following results were obtained in attempting to reproduce triethylphosphine from its oxide.

The oxide used was prepared by boiling triethylphosphine with concentrated nitric acid; the triethylphosphine is best made by Hofmann's method—the action of phosphorus trichloride on zinc ethyl. Another method was also used that gave a quantitative yield, namely, the action of heat on tetraethylphosphonium hydrate. The method recommended by Pickard and Kenyon (T., 1906, **89**, 262), namely, the action of Grignard's reagent on phosphoryl chloride, was also tried, but the yield was not good.

The oxide used in the following experiments was obtained pure by distillation. It boiled at 240°, and melted at 44°. Although sodium does not react with it at its boiling point, other metals were tried at higher temperatures. It was found, however, that unless the metals, zinc and magnesium, were heated to such a temperature that entire decomposition of the triethylphosphine oxide occurred, the substance distilled over the heated metals unchanged.

The next experiment was made with phosphorus pentachloride in the hopes that the oxygen might be displaced by chlorine. This was successful:

$$(C_2H_5)_3PO + PCl_5 = (C_2H_5)_3PCl_2 + POCl_3.$$

8·8 Grams of phosphorus pentachloride were added to 5·66 grams of the oxide, heat was evolved, and the oxide melted; finally, the mixture was heated, when phosphoryl chloride distilled, leaving a

residue that crystallised when cold. This residue when treated with water gave triethylphosphine oxide and hydrochloric acid. It also was found to be reduced in alcoholic solution by boiling with sodium amalgam, the characteristic odour of triethylphosphine being easily recognised. Enough triethylphosphine was prepared in this way to make a small quantity of tetraethylphosphonium iodide (Found, I = 46·1. $C_8H_{20}IP$ requires I = 46·3 per cent.).

The pure compound, $(C_2H_5)_3PCl_2$, could not be prepared from the residue, for on distillation much decomposition took place; it first darkened, and at 245—250° a considerable quantity of ethyl chloride and other inflammable gases was evolved; the distillate was partly crystalline, and contained free yellow phosphorus, and much carbon remained in the distilling flask. The distillate contained some triethylphosphine dichloride, for on treating it with sodium hydroxide a trace of the oxide was obtained. It also contained triethylphosphine hydrochloride, for a small quantity of triethylphosphine also was produced by the alkali. The dichloride therefore decomposes at its boiling point:

$$(C_2H_5)_3PCl_2 = (C_2H_5)_3P + Cl_2,$$

the free chlorine reacting with a further quantity, giving ethyl chloride, hydrogen chloride, and other decomposition products.

The distillate, therefore, was again distilled, but considerable decomposition occurred and carbon remained. An analysis was made of the substance that condensed in the receiver; it was found to contain Cl = 26·0, whilst $(C_2H_5)_3PCl_2$ requires Cl = 37·5 per cent. The distillate was obviously not triethylphosphine dichloride. The above determination of chlorine was made by dissolving the substance in water and adding silver nitrate; it was noticed that a certain amount of reduction took place unless nitric acid was added as well. This suggested that possibly another kind of decomposition had taken place during the distillation:

$$(C_2H_5)_3PCl_2 = (C_2H_5)_2PCl + C_2H_5Cl.$$

Monochlorodiethylphosphine contains Cl = 28·9 per cent. On adding water to it monohydroxydiethylphosphine would result, and this would easily oxidise to diethylphosphinic acid, $(C_2H_5)_2PO_2H$.

The remainder of the distillate was therefore treated with silver oxide and water, boiled and filtered, and the filtrate evaporated. A considerable quantity of a crystalline silver salt was obtained, consisting of fine needles. These were recrystallised and analysed; they contained no water of crystallisation.

Found: C = 20·4; H = 3·9; Ag = 47·9.

$C_4H_{10}O_2PAg$ requires C = 20·9; H = 4·4; Ag = 47·1 per cent.

The silver salt, however, was not quite pure, and during evaporation deposited a certain amount of metallic silver.

Another experiment, therefore, was made: the distillate from the compound produced by the action of phosphorus pentachloride on triethylphosphine oxide was added to dilute nitric acid, and the solution evaporated to dryness. The residue was then boiled with water and silver oxide, in excess, and filtered; the filtrate on evaporation gave a considerable amount of the silver salt. After recrystallisation it gave on analysis: C = 20·5; H = 4·2; Ag = 47·1 per cent. From the amount of silver salt produced the chief action of heat on triethylphosphine dichloride is to produce diethylphosphine monochloride and ethyl chloride. Phosphorus, therefore, in this respect behaves like bismuth, for triphenylbismuthine dichloride, even when boiled with benzene, decomposes into diphenylchlorobismuthine and chlorobenzene (Challenger and Allpress, P., 1914, **30**, 292).

Triethylphosphine, therefore, can be obtained from triethylphosphine oxide; also, a disubstituted phosphine compound has been prepared from a trisubstituted compound.

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[*Received Feb. 18th*, 1915.]

XLIV.—*Some Benzopyranol Derivatives.*

By JOHN NORMAN COLLIE and GERALD NOEL WHITE.

SOME years ago one of the authors (J. N. C., T., 1907, **91**, 1806) pointed out how the "keten" group $\cdot CH_2 \cdot CO \cdot$ could be regarded as a constituent of a very large number of interesting compounds:

Acetic acid, $H \cdot (CH_2 \cdot CO) \cdot OH$.

Diacetic acid, $H \cdot (CH_2 \cdot CO)_2 \cdot OH - CO_2 = H \cdot (CH_2 \cdot CO) \cdot CH_3$, acetone.

Triacetic acid, $H \cdot (CH_2 \cdot CO)_3 \cdot OH - CO_2 = H \cdot (CH_2 \cdot CO)_2 \cdot CH_3$, acetyl-acetone.

Tetra-acetic acid, $H \cdot (CH_2 \cdot CO)_4 \cdot OH - CO_2 = H \cdot (CH_2 \cdot CO)_3 \cdot CH_3$, diacetyl-acetone.

Not only can acetic acid be converted into the above compounds by simple reactions, but by further loss of water diacetylacetone yields according to the method employed either dimethylpyrone or orcinol; the former is a cyclic compound containing oxygen, the latter a benzene derivative; both these substances are representa-

tives of two important classes of organic compounds, namely, of pyrone and benzene. The following paper deals with a further simple condensation of these keten derivatives, namely, that of orcinol with acetylacetone:

$$C_7H_8O_2 + C_5H_8O_2 = C_{12}H_{12}O_2 + 2H_2O.$$

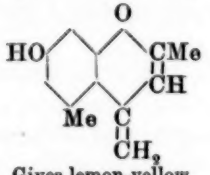
The whole series of reactions involved in the production of this compound, $C_{12}H_{12}O_2$, from acetic acid might therefore be summed up as follows:

$$7H\cdot[CH_2\cdot CO]\cdot OH = C_{12}H_{12}O_2 + 2CO_2 + 8H_2O.$$

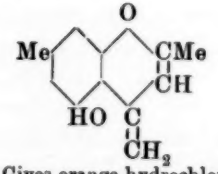
Orcinol and acetylacetone condense together with the greatest of ease when treated with concentrated hydrochloric or sulphuric acid; two compounds having the formula $C_{12}H_{12}O_2$ are formed; both are basic, and form salts with the excess of acid employed; one of the hydrochlorides is lemon-yellow, the other is orange in colour. The yield is 70 per cent. of the theoretical amount. The free bases can be obtained from the salts by the addition of sodium acetate, that of the lemon-yellow salt is deep orange, that of the orange salt is violet.

These substances are members of a series which have been called by Bülow (Bülow and Wagner, *Ber.*, 1901, **34**, 1189; Bülow, *Ber.*, 1903, **36**, 190; Bülow and Deiglmayr, *Ber.*, 1904, **37**, 1791, 4528) the 1:4-benzopyranols, and he points out that 1:4-benzopyranol is the parent substance of a new class of dyes, and is related to the natural dyes, apigenin, chrysin, and luteolin. These benzopyranol compounds are also related to the benzopyrylium compounds and the anthocyanin colours found in flowers.

The two compounds having the formula $C_{12}H_{12}O_2$ are thus *7-hydroxy-2:5-dimethyl-4-methylene-γ-benzopyranol* and *5-hydroxy-2:7-dimethyl-4-methylene-γ-benzopyranol*:

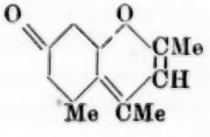


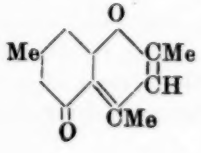
Gives lemon-yellow hydrochloride.



Gives orange hydrochloride.

There are alternative formulæ for the two substances, making them quinonoid in structure:





The fact, however, that both the substances can be acetylated is against this idea; moreover, many attempts were made to prepare quinonoid compounds with hydroxylamine, semicarbazide, and phenylhydrazine, but in no case were products obtained that were capable of isolation in the pure condition. The substances obtained were certainly not simple condensation products; in fact, with hydroxylamine the free bases gave end-products entirely free from nitrogen, whilst with phenylhydrazine only tarry compounds resulted, which spontaneously decomposed further even in solution. The evidence of a carbonyl group is therefore unsatisfactory. Moreover, if the substances are true quinones they should be easily reduced. They are not affected by sulphurous acid, but by continued boiling with concentrated hydrochloric acid and zinc or tin they are eventually converted into dihydro-compounds ($C_{12}H_{14}O_2$), but these compounds are not capable of being oxidised back again to the original substances ($C_{12}H_{12}O_2$) by ordinary oxidising agents.

Another point worthy of note is that both the acetyl derivatives and the dihydro-derivatives seem to have lost the power of forming salts with acids, at any rate when water is present. That the displacement of the hydroxyl group in the benzene nucleus by the acetoxyl group should entirely destroy the basic nature of the other half (the pyranol nucleus) is a fact difficult to explain. Moreover, there is another fact which the hydroxyl formula of Bülow does not explain. Both the two substances ($C_{12}H_{12}O_2$) have the same chromophoric system, and consequently should be similarly coloured.

Probably the best explanation is that the substances when in the form of salts or in the free state (produced by adding sodium acetate to the salts) are in the quinonoid condition, but the acetate not being quinonoid is colourless. If acids on the one hand favour the quinonoid form, bases on the other should promote the production of the hydroxyl form; hence with hydroxylamine, etc., no definite compounds would be formed, and it is a fact that both the orange and violet bases dissolve in sodium hydroxide solution, yielding solutions not so highly coloured even as the hydrochlorides; in fact, in the case of the violet base the solution is practically colourless.

Experimental.

Preparation of the Two Benzopyranol Compounds, $C_{12}H_{12}O_2$.

The action of concentrated hydrochloric acid on a solution of orcinol in acetylacetone containing a slight excess above the molecular quantity of the latter substance is found to give a mixture of two products. This condensation can also be effected

by passing dry hydrogen chloride through a solution of these two substances in a suitable solvent or by the action of concentrated hydrobromic acid or sulphuric acid. When the action is complete the mixed salts form a voluminous, crystalline mass, homogeneous in appearance. The hydrochlorides and hydrobromides of the benzopyranols are the best with which to work, for they can be separated moderately easily by fractional crystallisation. The yield is 70 per cent. of the theoretical.

Hydrochlorides of the Compounds $C_{12}H_{12}O_2$.

The two *hydrochlorides* are lemon-yellow and orange in colour, the two *hydrobromides* are greenish-yellow and orange.

The orange hydrochloride is most conveniently separated from the yellow isomeride by crystallisation from concentrated hydrochloric acid, in which it is less readily soluble, and may be isolated in the pure condition by three crystallisations. The yellow hydrochloride is crystallised most easily from dilute hydrochloric acid. The same applies to the hydrobromides, hydrobromic acid being an excellent solvent for separating the two salts. Unnecessary heating of the solution should be avoided as there is a tendency to decomposition into insoluble products.

The two salts both crystallise with one molecule of water of crystallisation; when this is removed by heating to 100° the remaining anhydrous salts are of a deeper colour than the hydrated salts.

An analysis of the hydrochlorides gave the following results:

	Orange salt.		Yellow salt.	$C_{12}H_{12}O_2,HCl,H_2O$
	I.	II.	I.	requires
C	59·2	59·1	59·0	59·3
H.....	6·5	6·1	6·1	6·2
Cl.....	14·7	14·6	14·5	14·7
H_2O... ..	7·9	8·0	7·5	7·4

The solutions of the two hydrochlorides are only very faintly acid to litmus paper. The molecule of water of crystallisation can be removed by heating to 100°; the anhydrous salts are deeper in colour than the hydrated salts. At 200° discoloration of the salts occurs, the decomposition being complete at 233—235°. The yellow hydrochloride often crystallises in wart-shaped crystals, the orange hydrochloride in double tufts of needles growing from a common centre.

The Free Bases, $C_{12}H_{12}O_2$.

These compounds can be prepared either by careful addition of an alkali, or better by addition of a solution of sodium acetate to

solutions of the hydrochlorides; they are insoluble in water. The base from the yellow hydrochloride is orange, that from the orange hydrochloride, violet. The orange base dissolves in alcohol in the ordinary way; the violet base gives a very pale brown solution, but when heated a deep violet colour is produced; this disappears again on cooling. Neither of the bases contains water of crystallisation.

Orange Base.—Found: C = 76·2; H = 6·5.

Violet Base.—Found: C = 76·1; H = 6·6.

$C_{12}H_{12}O_2$ requires C = 76·6; H = 6·4 per cent.

Both bases dissolve readily in sodium hydroxide solution; the orange base gives a yellow solution not strongly coloured, and the violet base gives an almost colourless solution.

Hydrobromides, $C_{12}H_{12}O_2$,HBr.

By the action of concentrated hydrobromic acid on a mixture of orcinol and acetylacetone two hydrobromides are produced. One is greenish-yellow and the other is orange in colour. They can be separated in the same way as the hydrochlorides by crystallisation from hydrobromic acid. The hydrobromides do not contain water of crystallisation.

Greenish-yellow Salt.—Found: Br = 29·6, 29·3.

Orange Salt.—Found: Br = 29·8.

$C_{12}H_{12}O_2$,HBr requires Br = 29·7 per cent.

Platinichlorides.—When a warm solution of chloroplatinic acid is added to a warm solution of either of the hydrochlorides in dilute hydrochloric acid, a crystalline, yellow precipitate of the *platinichloride* is produced. It can be obtained pure by merely washing with a little cold dilute hydrochloric acid and drying in a vacuum.

Found: Pt = 24·8 (from yellow hydrochloride).

Found: Pt = 24·8 (from orange hydrochloride).

$(C_{12}H_{12}O_2)_2$,H_2PtCl_6 requires Pt = 24·8 per cent.

When a solution of the above salts, or the mother liquors obtained in the preparation of the above salts, is boiled, some chlorine is evolved, and on cooling crystals separate; prolonged boiling even produces some metallic platinum. These crystals are *platinochlorides.*

Found: Pt = 27·2 (from yellow hydrochloride).

Found: Pt = 27·2 (from orange hydrochloride).

$(C_{12}H_{12}O_2)_2$,H_2PtCl_4 requires Pt = 27·2 per cent.

This loss of halogen occurs more easily in the case of the hydrobromide, for if the hydrobromide is used in place of the hydro-

chloride in the above preparation a heavy, yellowish-brown precipitate is produced.

Found: Pt = 59·2 (from yellowish-green hydrobromide).

Found: Pt = 58·8 (from orange hydrobromide).

The precipitate was found to contain metallic platinum.

Perchlorates.

A great difference in solubility exists between the greenish-yellow and the orange perchlorates. The orange salt is sparingly soluble in cold aqueous perchloric acid, whilst the yellowish-green salt dissolves readily. This can be used as a method for separating the orange salt from a mixture of the two, but the more readily soluble greenish-yellow salt cannot be obtained from the mother liquor on evaporation by warming, for decomposition at once occurs. By adding sodium acetate to these mother liquors the orange base of the yellowish-green salt is precipitated, and can be further purified. The two perchlorates were prepared by dissolving the bases in perchloric acid and crystallising. On heating they deflagrate with considerable violence. The orange salt contains water of crystallisation. The chlorine in them was determined by reduction of the salts in sodium hydroxide solution by hydrazine sulphate, acidifying with nitric acid, and precipitating with silver nitrate.

Orange Salt.—Found: Cl = 11·2, 10·9.

Greenish-yellow Salt.—Found: Cl = 11·8.

$C_{12}H_{12}O_2,HClO_4$ requires Cl = 12·3 per cent.

The orange salt obviously contains water of crystallisation:

$C_{12}H_{12}O_2,HClO_4,2H_2O$ requires Cl = 10·9 per cent.

A determination of the water of crystallisation was made by leaving the salt in a vacuum over phosphoric oxide for some days.

Found: H_2O = 11·0.

$C_{12}H_{12}O_2,HClO_4,2H_2O$ requires H_2O = 11·1 per cent.

Mercury Chloride Compounds.

If mercuric chloride solution is added to an alcoholic solution of either of the two bases, coloured, insoluble compounds are precipitated. The product is a mixture of mercuri- and mercurochlorides. These can be separated by means of cold pyridine, which dissolves the mercurichloride, leaving the mercurochloride as an insoluble residue identical in colour with the mercurochloride. The mercuric salt of the orange base is a deep orange colour, whilst that of the violet base is a purplish-red colour. The

solutions of them in pyridine are deeper in colour than the solids, being crimson and violet respectively.

The compounds are reduced with the greatest ease; in the cold they will oxidise ethyl alcohol to acetaldehyde, and become mercurochlorides. On boiling with alcohol mercury is deposited. Mineral acids at once displace the mercury chloride.

Orange Salt.—Found: Hg = 30·7.

Purple Salt.—Found: Hg = 30·3.

$(C_{12}H_{12}O_2)_2,HgCl_2$ requires Hg = 30·8 per cent.

The mercurochlorides can be obtained either during the preparation of the mercurichloride or by warming a dilute solution of the mercurichloride in aqueous alcohol to about 50°. It should be quite insoluble in pyridine.

Orange Salt.—Found: Hg = 61·3.

Purple Salt.—Found: Hg = 60·5.

$C_{12}H_{12}O_2,Hg_2Cl_2$ requires Hg = 60·7 per cent.

Dihydro- and Tetrahydro-compounds.

When either of the two hydrochlorides is reduced in hydrochloric acid solution by metallic zinc, reduction gradually takes place on boiling. The reduction product separates as a viscous mass clogging the zinc. After the solution becomes colourless the reduced product can be dissolved in hot alcohol and again precipitated by pouring into water. It is colourless, insoluble in acids, soluble in alkali, and could not be obtained in a crystalline condition.

It seems, however, to have very faintly basic properties, for if dissolved in dry benzene, and dry hydrogen chloride is passed into the solution a cream-coloured hydrochloride separates; on warming, the substance is decomposed with loss of hydrogen chloride.

The dihydro-compounds are oxidised in the air only after long exposure.

From Yellow Salt.—Found: C = 74·6; H = 7·5.

From Orange Salt.—Found: C = 75·7; H = 7·4.

$C_{12}H_{14}O_2$ requires C = 75·7; H = 7·4 per cent.

A further reduction can be effected by the use of aluminium amalgam. The dihydro-compound produced from the yellow salt gave a *tetrahydro*-compound by this method. In appearance and properties it differed little from the dihydro-compound, but it formed no additive products with hydrogen chloride.

Found: C = 75·0; H = 8·2.

$C_{12}H_{16}O_2$ requires C = 75·0; H = 8·3 per cent.

Attempts were made to produce some crystalline compounds of these dihydro-compounds. The bromo-compounds are amorphous; the *nitro*-compounds, however, crystallise in minute needles. They were prepared from the dihydro-compounds by nitrating in glacial acetic acid.

The substances are soluble in alcohol; they also dissolve in alkalis with a yellow colour; at 100° decomposition takes place.

From Yellow Salt.—Found: N = 5·2.

$C_{12}H_{13}O_4N$ requires N = 5·9 per cent.

From Orange Salt.—Found: N = 9·4. Equiv. = 278.

$C_{12}H_{12}O_6N_2$ requires N = 9·6 per cent. Equiv. = 280.

Many attempts were made with the two bases ($C_{12}H_{12}O_2$) to prepare compounds with hydroxylamine, semicarbazide, etc., but without success. Reaction occurs because the solutions become nearly colourless. In the case of hydroxylamine only products free from nitrogen were obtained. By the action of semicarbazide a non-crystalline compound was obtained from the base of the yellow salt; it contained N = 7·3. This may be an iminoquinone compound, $C_{12}H_{12}O{\cdot}NH$, which requires N = 7·4 per cent.

A few experiments were made on the condensation products obtained by treating a mixture of phloroglucinol and acetylacetone with fuming hydrochloric acid. An excess of acetylacetone was used. On the addition of the fuming hydrochloric acid a bright yellow precipitate was soon formed. This was collected, and the mother liquor, on keeping, deposited an orange salt. Both salts were recrystallised from hot water.

Yellow Salt.—Found: C = 58·0; H = 4·8; Cl = 15·8.

$C_{11}H_{10}O_3$,HCl requires C = 58·3; H = 4·8; Cl = 15·7 per cent.

Orange Salt.—Found: C = 58·3; H = 4·4; Cl = 10·5.

$C_{17}H_{14}O_5$,HCl requires C = 58·2; H = 4·3; Cl = 10·6 per cent.

The orange salt is therefore a condensation product, not of phloroglucinol itself, but of phloroglucide.

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[*Received Feb.* 18*th*, 1915.]

XLV.—*Influence of Sucrose and Alkali Chlorides on the Solvent Power of Water.*

By James Charles Philip and Arthur Bramley.

In papers published some years ago (T., 1907, **91**, 711; *Trans. Faraday Soc.*, 1907, **3**, 140) one of the authors directed attention to the influence of various substances on the solubility of gases in water, and developed the suggestion, already thrown out in a general way by other workers, that this effect is connected with the hydration of these added substances. It was clearly shown that, contrary to the view held in some quarters, the solubility of a non-electrolyte in water may be affected to a notable extent by the presence of another non-electrolyte, and an attempt was made to calculate the average molecular hydration of sucrose in aqueous solution from the influence which this substance has in lowering the solubility of hydrogen in water. The influence of salts also was treated from the same point of view.

Whether the supposed hydration of the added substance is regarded as offering an adequate interpretation of the lowered solvent power of water for non-electrolytes or not, it is a matter of great interest to ascertain how the magnitude of the effect varies with the nature of the added substance, and to find how far it is independent of the particular non-electrolyte which is employed in measuring the solvent power of the water. It was with the object of throwing further light on this problem that the experiments described in this paper were carried out.

Since the publication of the earlier communications (*loc. cit.*) further experimental data bearing on the influence of non-electrolytes on the solubility of gases in water have become available (Usher, T., 1910, **97**, 66; Drucker and Moles, *Zeitsch. physikal. Chem.*, 1910, **75**, 405; Müller, *ibid.*, 1912, **81**, 483). The bearing of this work on the problem in question will be discussed in connexion with the results of the present investigation.

Gases are not the only non-electrolytes the solubility of which in water has been studied from the point of view developed in the foregoing paragraphs. Euler (*Zeitsch. physikal. Chem.*, 1899, **31**, 360) and Lundén (*Medd. K. Vetensk. Nobelinst.*, 1911, **2**, No. 15) have investigated the influence of salts on the solubility of ethyl acetate in water, the latter author regarding the phenomenon as a manifestation of neutral salt action. Rothmund (*Zeitsch. physikal. Chem.*, 1900, **33**, 401) and Biltz (*ibid.*, 1903, **43**, 41) have studied in a similar manner the effect of salts on the solubility of phenylthiocarbamide.

Analogous experiments have been made by Euler (*Zeitsch. physikal. Chem.*, 1904, **49**, 303) with aniline and ethyl ether, and by McLauchlan (*ibid.*, 1903, **44**, 600) with iodine.

A compound, the solubility of which is to be taken as a measure of the solvent power of water in the presence of different added substances, must fulfil certain conditions. It should be indifferent, incapable of reacting with or being dissolved by, the added substance, sparingly soluble, and susceptible of accurate estimation. The number of non-electrolytes which satisfy these requirements, even approximately, is exceedingly small. Ethyl acetate, the compound employed by Euler and Lundén, whilst satisfactory in most respects, is open to the objection that its solubility is fairly high; its saturated solution, at the ordinary temperature, contains about 0·8 gram-molecule per litre. Phenylthiocarbamide is probably not quite indifferent to alkali salts, and the experiments of Bogdan (*Ann. Sci. Univ. Jassy*, 1903, **2**, 95) show that this substance is more soluble in solutions of non-electrolytes than in pure water, indicating that the solvent power of the non-electrolytes themselves for phenylthiocarbamide may be considerable. As regards aniline and ethyl ether, the difficulty of accurate estimation militates against their use, whilst iodine can scarcely be regarded as an indifferent substance.

In these circumstances it was thought advisable to employ the distribution method, and the work recorded in this communication is therefore a study of the variation in the partition coefficient of a suitable indifferent compound between an organic liquid (benzene or petroleum) and aqueous solutions of sucrose or alkali chlorides. The advantage of this method is that the concentration of the distributed compound can be kept as low as desirable, consistent with accuracy in its estimation. As distributed substance we have used ethyl acetate, phenol, and acetone. These compounds are all capable of accurate estimation in aqueous solutions even at low concentrations. As regards the other requisite conditions enumerated above, ethyl acetate is the most satisfactory of the three, since the available evidence indicates that the disturbance arising from the solvent power of the added substance (sucrose or alkali chloride) is probably least in this case. The significance of this factor will be discussed in connexion with the results obtained with the different distributed substances.

Dawson and McCrae (T., 1901, **79**, 493) and Dawson (*Zeitsch. physikal. Chem.*, 1906, **56**, 605) have already employed the distribution method in the study of similar problems, but the distributed substances used, namely, ammonia and iodine, can scarcely be regarded as indifferent. A series of experiments, analogous

to those described in this paper, was made by Rothmund and Wilsmore (*Zeitsch. physikal. Chem.*, 1902, **40**, 624), who studied the influence of potassium sulphate on the partition of phenol between benzene and water.

Experimental.

As already stated, the distributed substances used were ethyl acetate, phenol, and acetone. The quantity of ethyl acetate present in aqueous solution was estimated by adding excess of standard sodium hydroxide solution, keeping for a sufficient time, and then titrating back with standard hydrochloric acid. The estimation of ethyl acetate in benzene or petroleum solution was carried out in the same way, except that a standard alcoholic solution of potassium hydroxide was employed for hydrolysis.

Phenol in aqueous solution was determined by conversion into tribromophenol, the actual procedure followed being that described by Redman, Weith, and Brock (*J. Ind. Eng. Chem.*, 1913, **5**, 389). Phenol in benzene solution was estimated by extracting three times with an equal volume of 2·5*N*-sodium hydroxide, acidifying the united extracts, and converting into tribromophenol as before. The accuracy of this procedure was tested and found to be satisfactory (compare Rothmund and Wilsmore, *loc. cit.*).

In the determination of acetone, whether in water or benzene solution, Messinger's method was employed (see Marriott, *J. Biol. Chem.*, 1913, **16**, 281). It was found that when an iodine solution is treated with alkali in large excess, and is then acidified, the quantity of iodine liberated, as estimated by standard thiosulphate, is slightly less than that originally taken. This discrepancy is being further studied, but for the purposes of the present investigation a suitable correction, based on blank experiments, was introduced.

In the experiments on the partition of ethyl acetate between benzene and water, pure commercial benzene was employed, but in those with phenol and acetone benzene specially purified by treatment with concentrated sulphuric acid and by redistillation was used, because of the complications that otherwise arose in the estimation of the distributed substances. Test experiments showed that the partition coefficient of ethyl acetate was the same whether pure commercial benzene or the specially purified product was used. The boiling point of the petroleum employed was 90—110°; the partition coefficient, however, for ethyl acetate varied slightly from one lot of petroleum to another, and care was therefore taken to use the same petroleum throughout each series of experi-

ments. The ethyl acetate, phenol, and acetone were all specially purified samples, boiling within 0·1°.

In the case of each of the three distributed substances, experiments were made to test the constancy of the partition coefficient over a considerable range of concentration. The data bearing on this point are reproduced in the following tables, in which C_w is the concentration (grams per litre) of the distributed substance in the aqueous layer, and P is the partition coefficient, that is, the ratio:

$$\frac{\text{concentration in benzene (petroleum) layer}}{\text{concentration in aqueous layer.}}$$

Ethyl Acetate between Benzene and Water at 20°.

C_w	2·480	1·629	1·590	1·472	1·199	0·805
P	12·23	12·19	12·16	12·19	12·21	12·24

Ethyl Acetate between Petroleum and Water at 25°.

C_w	3·339	3·098	2·943	2·674	2·561	2·335	2·122	1·924
P	3·442	3·435	3·453	3·450	3·430	3·454	3·453	3·457

Phenol between Benzene and Water at 20°.

C_w	0·945	0·888	0·711	0·594	0·475	0·356	0·238	0·119	0·0601
P	2·194	2·189	2·184	2·176	2·181	2·173	2·175	2·180	2·189

Acetone between Benzene and Water at 20°.

C_w	0·375	0·302	0·227	0·153
P	0·833	0·827	0·832	0·839

The mean values of the partition coefficient of ethyl acetate between benzene and water at different temperatures were found to be:

Temp.	11·9°	20·0°	25·0°	30·0°	40·0°
P.	10·66	12·20	13·10	13·95	15·61

So far as we can find, the partition coefficient of ethyl acetate between benzene and water has not been determined previously, but data are already on record for the distribution of phenol and acetone between these two solvents. Rothmund and Wilsmore (*Zeitsch. physikal. Chem.*, 1902, **40**, 611) determined the partition coefficient of phenol between benzene and water at 25° over a wide concentration range, and found values falling from 12·24 to 2·29, the corresponding concentrations of the aqueous layers being 49·8 and 2·56 grams of phenol per litre respectively. We find that the partition coefficient at 20°—mean value 2·182—is independent of the concentration, but it should be borne in mind

that our range of concentration—0·945 to 0·0601 gram of phenol per litre of the aqueous layer—is quite different from that covered by Rothmund and Wilsmore's experiments, and, further, even the figures given by these investigators show that the value of P is falling off much less rapidly at the lower concentrations. The temperatures also are different.

As regards the partition coefficient of acetone between benzene and water, Herz and Fischer find values of P at 25°, which range from 1·080 to 0·938, the corresponding concentrations of the aqueous layers being 128·6 and 12·76 grams of acetone per litre respectively. We find a practically constant figure for P at 20°—mean value 0·833—over a range of concentrations which are very much lower than those employed by Herz and Fischer.

The influence of sucrose on the distribution of ethyl acetate between benzene (or petroleum) and water is shown in the tables below. In these, N represents the concentration of the sucrose solution in gram-molecules per 1000 grams of water, and P is the partition coefficient, as defined already. S_v, calculated from the values of P, represents the *relative* quantities of ester present in 1 litre of the aqueous layers, the quantity present in 1 litre of water at the same temperature, and in equilibrium with the same benzene or petroleum solution, being taken as unity. S_w represents the relative quantities of ester present in those volumes of different solutions which contain 1000 grams of water, the quantity present in 1 litre of pure water at the same temperature and in equilibrium with the same benzene or petroleum solution being taken as unity. The fifth column, under the heading $(1-S_w)/N$, gives the values of what may be described as the "equivalent relative lowering of solvent power." The concentrations of ethyl acetate employed in these experiments were almost all within the range indicated in the tables on p. 383.

It is clear that in taking S_w as a measure of the solvent power of 1000 grams of water in the presence of different quantities of sucrose, the assumption is made that the sucrose itself does not dissolve any of the ethyl acetate. Since sucrose is insoluble in ethyl acetate, as we have found by experiment, there is a strong presumption that the solubility of ethyl acetate in sucrose is negligibly small. If the assumption were not valid, that is, if the sucrose were able to dissolve ethyl acetate, then the tabulated values of S_w, which are taken as measuring the solvent power of the water alone, are too high, and the values of $(1-S_w)/N$ are too low. In other words, the values of the equivalent relative lowering of the solvent power of water, calculated on the assumption that the added substance (sucrose) has no solvent power of its

own, are minimum values (compare Philip, *Trans. Faraday Soc.*, 1907, **3**, 145; Caldwell, *ibid.*, 158). There are no doubt many cases where the assumption is not valid (compare Usher, T., 1910, **97**, 66), and that circumstance indicates the necessity of considering each case on its merits.

Distribution of Ethyl Acetate between Petroleum and Sucrose Solutions at 20°.

N.	P.	S_v.	S_w.	$(1-S_w)/N$.
0·00	3·13	1·000	1·000	—
0·559	3·90	0·802	0·898	0·18
1·270	5·06	0·618	0·786	0·17
2·204	6·86	0·456	0·671	0·15
3·496	9·32	0·336	0·588	0·12

This table will serve to show in detail how the values of the equivalent relative lowering of solvent power have been ascertained, and the other results obtained for the influence of sucrose on the partition of ethyl acetate between petroleum (or benzene) and water may be communicated in a somewhat abbreviated form. It will be sufficient to indicate for each series the nature of the organic solvent used, and the temperature.

	Petroleum at 8·7°		Benzene at 11·9°		Petroleum at 16·5°	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	2·40	—	10·66	—	2·85	—
0·559	3·03	0·205	13·72	0·235	3·69	0·245
1·270	4·03	0·195	17·37	0·175	4·81	0·195
2·204	5·65	0·17	23·84	0·155	6·59	0·165
3·496	8·21	0·114	—	—	9·11	0·13

	Petroleum at 22·5°		Petroleum at 25°	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	3·24	—	3·45	—
0·559	4·07	0·195	—	—
1·270	5·25	0·17	5·52	0·16
2·204	7·00	0·145	7·24	0·135
3·496	9·60	0·115	—	—

	Benzene at 30°		Benzene at 40°	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	13·95	—	15·55	—
0·559	—	—	18·9	0·13
1·270	21·4	0·13	22·6	0·095
2·204	27·4	0·115	29·4	0·10
3·496	—	—	34·9	0·06

The influence of sodium, potassium, and lithium chlorides on the distribution of ethyl acetate, phenol, and acetone between benzene and water at 20° has also been investigated, and the results are communicated in the following tables. The significance of the

symbols employed will be clear from the explanations already given in connexion with the experiments on sucrose solutions.

Sodium Chloride Solutions.

	Ethyl Acetate		Phenol		Acetone	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	12·20	—	2·182	—	0·833	—
0·506	14·75	0·32	2·615	0·305	0·938	0·20
1·02	17·72	0·29	3·16	0·29	1·056	0·19
1·55	21·4	0·265	3·84	0·265	1·193	0·18
2·08	25·7	0·245	4·66	0·245	1·342	0·17
3·196	36·9	0·20	6·77	0·205	1·705	0·15
4·37	51·6	0·17	10·04	0·175	2·13	0·13

Potassium Chloride Solutions.

	Ethyl Acetate		Phenol		Acetone	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	12·20	—	2·182	—	0·833	—
0·508	14·6	0·295	2·51	0·23	0·928	0·175
1·031	17·3	0·265	2·92	0·225	1·038	0·17
1·572	20·6	0·24	3·43	0·21	1·166	0·16
2·13	24·4	0·22	4·03	0·20	1·32	0·155
3·31	34·1	0·185	5·30	0·165	1·645	0·135
4·58	47·1	0·155	6·93	0·14	2·16	0·12

Lithium Chloride Solutions.

	Ethyl Acetate*		Phenol		Acetone	
N.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.	P.	$(1-S_w)/N$.
0·00	3·075	—	2·182	—	0·833	—
0·505	3·56	0·255	2·635	0·325	0·896	0·12
1·02	4·09	0·23	3·15	0·285	0·975	0·125
1·546	4·68	0·21	3·68	0·25	1·050	0·12
2·08	5·33	0·19	4·18	0·22	1·145	0·115

* These experiments were made with petroleum as the organic solvent instead of benzene.

A series of experiments made on the partition coefficient of ethyl acetate between petroleum and sodium chloride solutions at 20° is interesting, as showing that the values obtained for the equivalent relative lowering of solvent power are the same whether benzene or petroleum is used as the organic solvent. On comparing the following table with the corresponding one above the close agreement in the values of $(1-S_w)/N$ will be apparent.

Ethyl Acetate between Petroleum and Sodium Chloride Solutions at 20°.

N.	P.	$(1-S_w)/N$.
0·0	3·075	—
0·506	3·72	0·32
1·02	4·51	0·30
1·55	5·44	0·27
2·08	6·59	0·245

Discussion of Results.

The results recorded on p. 381, showing the influence of sucrose on the partition of ethyl acetate between benzene and water, emphasise the conclusion, already reached in the earlier communications, that the solvent power of water for a non-electrolyte may be affected to a notable extent by the presence of another non-electrolyte. This is quite opposed to Levin's view (*Zeitsch. physikal. Chem.*, 1906, **55**, 517) that solubility influences are appreciable only when ions are involved.

The values tabulated for $(1-S_w)/N$, the equivalent relative lowering of solvent power, exhibit a distinct increase with dilution in practically every case, whether the added substance is sucrose or an alkali chloride. This fact warrants the conclusion that whatever is the cause of the diminished solvent power of water in the presence of the added substance, it is some factor which becomes relatively more important as the proportion of water increases. In view of this, it does not seem to us permissible to calculate a *mean* value for the equivalent relative lowering of solvent power, as some authors have done under the impression that this quantity does not vary with the dilution of the added substance. Further, our results are opposed to Levin's contention (*loc. cit.*, p. 535) that solubility influences, such as those recorded above, are a phenomenon essentially of *concentrated* solutions.

It is instructive to compare our observations on the partition of ethyl acetate between benzene (or petroleum) and sucrose solutions with Müller's results (*Zeitsch. physikal. Chem.*, 1912, **81**, 483) for the influence of sucrose on the solubility of hydrogen, nitrogen, and oxygen in water at 15°. In order to facilitate the comparison, we have calculated from Müller's figures the equivalent relative lowering of solvent power in the way already described. The numbers under N represent gram-molecules of sucrose per 1000 grams of water:

Hydrogen.		Nitrogen.		Oxygen.	
N.	$(1-S_w)/N$.	N.	$(1-S_w)/N$.	N.	$(1-S_w)/N$.
0·504	0·23	0·376	0·16	0·403	0·13
0·743	0·14	0·731	0·175	0·943	0·165
1·245	0·13	1·25	0·17	1·16	0·17
1·36	0·14	1·26	0·15	2·20	0·14
1·92	0·12	2·69	0·10	2·84	0·125
2·20	0·125	2·76	0·125	2·92	0·12

These results are by no means regular, but, on the whole, the equivalent relative lowering of solvent power increases with the dilution of the sucrose. Further, the range covered by the values of $(1-S_w)/N$ is very nearly the same whether the reference substance for the solvent power of water in presence of sucrose is hydrogen, nitrogen, oxygen (as in Müller's experiments), or ethyl acetate (as in ours). This shows that the effect is primarily determined by some factor involved in the relation of the sucrose and the water, and only secondarily, if at all, by the specific character of the reference substance.

It should be noted that the values of the equivalent relative lowering of solvent power deduced from Müller's measurements and from the work recorded in this paper are somewhat higher than the values calculated from Steiner's data for the influence of sucrose on the solubility of hydrogen in water. These data were used by one of us (*loc. cit.*) in an attempt to calculate the average molecular hydration of sucrose, and gave for this quantity figures between 5·4 and 6·5. The average molecular hydration can be obtained from $(1-S_w)/N$ by multiplying by 1000/18, and if the range of values of $(1-S_w)/N$ recorded above for sucrose solutions is taken as 0·20—0·12 at ordinary temperatures, this would correspond with an average molecular hydration ranging from 11 for the more dilute solutions to 6·5 for the more concentrated ones. These figures are distinctly higher than those hitherto regarded as most probable.

Of the results deduced for the influence of alkali chlorides on the solvent power of water, those obtained with sodium chloride appear to us to be the most trustworthy. This salt, of all those employed in this investigation, is the least soluble in any of the distributed substances, ethyl acetate, phenol, or acetone, and it may therefore be presumed that any disturbance arising from the solvent power of the salt itself is at a minimum in this case. Further, for the sodium chloride solutions, the values obtained for the equivalent relative lowering of solvent power are the same whether the distributed substance is ethyl acetate or phenol. This circumstance, although not furnishing absolute proof, is strong evidence in favour of the view that the values of $(1-S_w)/N$ deduced

from the experiments with either of those distributed substances are a real measure of the extent to which the solvent power of the water has been affected by sodium chloride. Again, as pointed out on p. 381, the values deduced as above for the equivalent relative lowering of solvent power are minimum values, and hence the highest set of values obtained for $(1-S_w)/N$ is to be regarded as in all probability the best measure of the lowered solvent power. These values lie between 0·17 for a $4N$-solution of sodium chloride and 0·32 for a $0{\cdot}5N$-solution. Hence, on the assumption that the lowered solvent power of water in this case is due to the hydration of the molecules and ions of sodium chloride, the average molecular hydration would lie between 9·5 (for a $4N$-solution) and 17·8 (for a $0{\cdot}5N$-solution).

In the case of the potassium chloride solutions the agreement between the values of $(1-S_w)/N$ deduced from experiments (1) with ethyl acetate, (2) with phenol, is not quite so good, that is, the values of the equivalent relative lowering are not quite independent of the distributed substance. The figures resulting from the phenol experiments are somewhat lower than the corresponding ones based on the ethyl acetate experiments. We give the preference to the latter, on the general grounds already stated, and also on account of our observation that whilst both sodium and potassium chlorides are insoluble in ethyl acetate, phenol, in which sodium chloride is insoluble, dissolves a very small, but recognisable, quantity of potassium chloride. On the basis, then, of the ethyl acetate experiments, the value of the equivalent relative lowering of the solvent power of water in presence of potassium chloride rises from 0·155 for a $4N$-solution to 0·295 for a $0{\cdot}5N$-solution. On the hydration hypothesis these figures indicate an average molecular hydration of 8·6 molecules and 16·4 molecules respectively, that is, somewhat below the corresponding numbers for sodium chloride. It should be noted also that the values deduced in this paper for the average molecular hydration are for both salts rather higher than those previously calculated from their influence on the solubility of hydrogen in water.

It will be observed that the values of $(1-S_w)/N$ recorded for the partition of acetone between benzene and sodium or potassium chloride solutions are very much lower than those obtained with ethyl acetate or phenol as the distributed substance. We find that both chlorides are distinctly soluble in acetone, and the use of this compound as reference substance is therefore open to objection. In any case, the values of $(1-S_w)/N$, based on the partition of acetone between benzene and sodium or potassium chloride

solutions, cannot be taken as a real measure of the lowering of the solvent power of water in the presence of these salts.

Consideration of the data obtained with lithium chloride solutions has convinced us that here also the values deduced for $(1-S_w)/N$ are not to be regarded as giving a correct measure of the lowering of the solvent power of water. We find that all the three distributed substances, ethyl acetate, phenol, and acetone, especially the last-mentioned, are able to dissolve considerable quantities of lithium chloride, and this fact makes it probable that the solvent power of the salt itself for any of the three compounds is appreciable. If this is so, then the influence of lithium chloride on the solvent power of water cannot be estimated with any certainty by the method adopted in the case of sodium and potassium chlorides. The solvent power of lithium chloride itself being appreciable, it follows that the values of $(1-S_w)/N$ in this case are too low, and understate the influence of the salt on the solvent power of water. Hence the calculated values of the average molecular hydration would also be too low. On the basis of the phenol experiments with lithium chloride solutions, the average molecular hydration of this salt would be nearly the same as for sodium chloride. It is certain, however, on the ground of other experimental data, that the lithium salt is more highly hydrated than the sodium salt (see Washburn, *Technology Quart.*, 1908, **21**, 386).

It is desirable to elucidate further the factors which determine the solvent power of water in presence of added substances, and it is our purpose to continue the inquiry on the lines described in this communication.

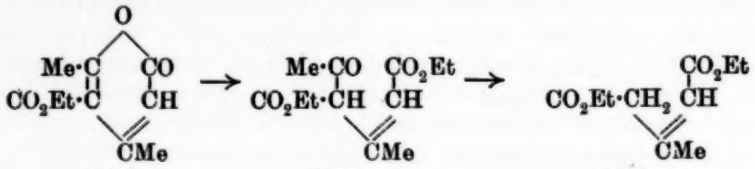
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.
SOUTH KENSINGTON, S W. [*Received March 1st*, 1915].

XLVI.—*The Formation of Coumarin Derivatives and the Preparation of Stable Coumarinic Acids.*

By LOUIS ARNOLD JORDAN and JOCELYN FIELD THORPE.

IN a former communication (T., 1912, **101**, 1557) it was shown that when ethyl *iso*dehydracetate (I) is treated with cold alcoholic sodium ethoxide it is converted, in the first instance, into the

acetyl derivative (II), and then into the labile modification of ethyl β-methylglutaconate (III):

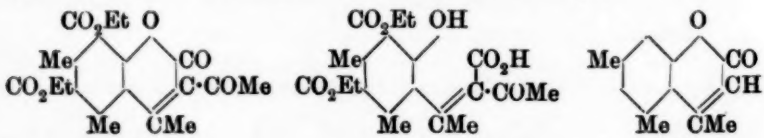


(I.) (II.) (III.)

It was then stated that the large quantity of acid material which is formed in this reaction can be converted to the extent of about one-half into the above labile ester (III) on esterification, but that considerable quantities of a neutral substance, melting at 134°, could also be isolated.

An analysis of this compound yielded numbers that suggested the formula $C_{12}H_{12}O_4$; it dissolved in alkali hydroxides, and the acid, precipitated by cautiously acidifying the alkaline solution, was found to melt at 141°, and to have the formula $C_{12}H_{14}O_5$. Since the last-named substance was reconverted into the compound melting at 134° when heated, it was concluded that the two substances were related to one another as acid and anhydride, but no further evidence could then be obtained which threw any light on their structure. Since that time, considerable quantities of the compound, melting at 134°, have been obtained, and we have been able to subject it to a thorough investigation. The substance, which melts when pure at 135°, has the empirical formula $C_{20}H_{22}O_7$, and the compound formed from it by the action of potassium hydroxide, which melts at 146°, has the composition $C_{20}H_{24}O_8$.

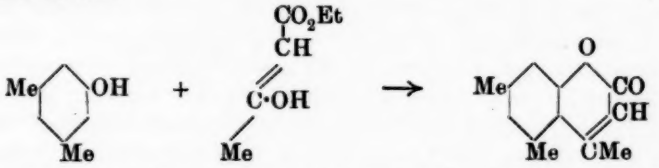
The compound melting at 146° gives a deep coloration with ferric chloride, a reaction which is not given by the neutral substance melting at 135°; the two compounds are therefore related to one another as lactone and hydroxy-acid. Their structure was revealed by the fact that, when completely hydrolysed, they were both converted into 4 : 5 : 7-trimethylcoumarin (VI). The compound melting at 135° is, therefore, ethyl 3-acetyl-4 : 5 : 7-trimethylcoumarin-6 : 8-dicarboxylate (IV), and the compound melting at 146° is the corresponding coumarinic acid (V):



(IV.) (V.) (VI.)

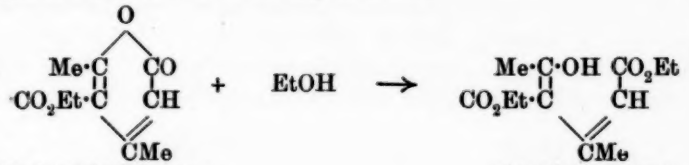
The identity of our coumarin with the compound prepared by the

condensation of *m*-5-xylenol and ethyl acetoacetate in accordance with the scheme



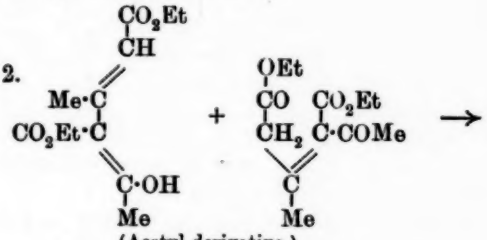
was proved by a direct comparison rendered possible by the kindness of Dr. Clayton in sending us a specimen of the compound prepared by him (T., 1908, **93**, 2020). It is evident, therefore, that the substance melting at 135° is formed from ethyl *iso*-dehydracetate, in the following manner:

1.

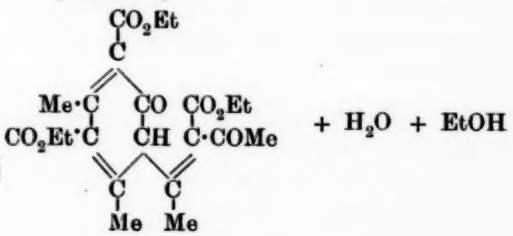


(Ethyl *iso*dehydracetate.) (Acetyl derivative.)

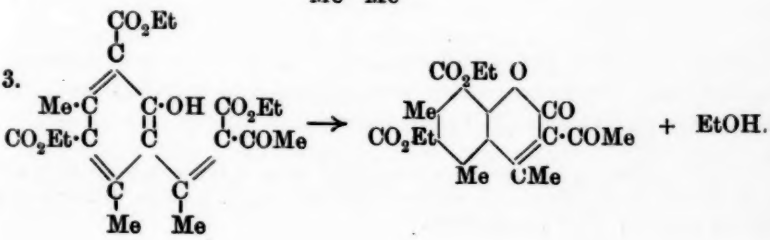
2.



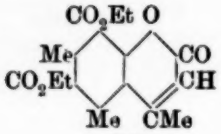
(Enol form.) (Acetyl derivative.) (Keto form.)



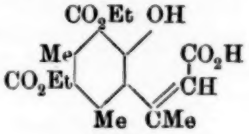
3.



Several interesting features arise out of the study of the coumarins described in this communication. In the first place, the remarkable stability of the coumarinic acids is worthy of notice. The transformation of coumarins into stable coumarinic acids has only been observed, hitherto, in the case of certain nitrocoumarins, and especially with those compounds which contain the nitro-group in the position 8. The coumarinic acids described in this paper are relatively stable substances, yet the stability evidently decreases with the decrease in the number of substituents in the benzene nucleus, and is greatest when the position 8 is occupied by the carboxyl group. The formation of the coumaric acids could not be effected. Again, the acetyl group in position 3 is characterised by possessing most unexpected stability towards alkali.* The presence of this group is proved by the fact that it can be estimated by the Perkin method, and is entirely removed by alcohol and sulphuric acid, the product being the coumarin (VII), from which the corresponding coumarinic acid (VIII) can be prepared:



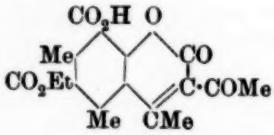
(VII.)



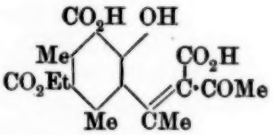
(VIII.)

This coumarinic acid does not differ appreciably in stability from the compound containing the acetyl group, and it is evident that this complex has little effect on the closing of the ring.

It is towards alkali that the remarkable stability of the acetyl compound is exhibited, and the only effect of fused alkali on the compound melting at 135° is to hydrolyse one carbethoxy-group, yielding the coumarin (IX), from which the coumarinic acid (X) can be prepared:



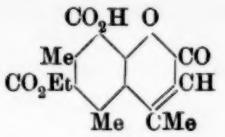
(IX.)



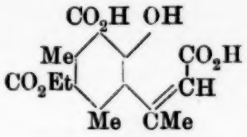
(X.)

That the acetyl group still remains in these substances is proved by the fact that when treated with alcohol and sulphuric acid the compounds (XI) and (XII) are formed:

* This stability is all the more remarkable when it is remembered that the corresponding 3-nitro-derivatives react at once with alkali forming derivatives of styrene (Clayton, *T.*, 1910, **97**, 1392).



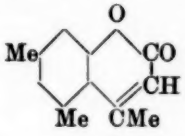
(XI.)

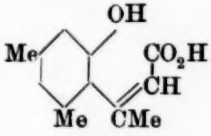


(XII.)

Prolonged action of concentrated alkali appears to have no effect on the carbethoxy-group in position 6, and the stability of this group must be ascribed to the presence of the two ortho-methyl groups, in accordance with the Victor Meyer law.

On the other hand, concentrated aqueous sulphuric acid causes complete hydrolysis to 4 : 5 : 7-trimethylcoumarin, and it is interesting to note that the corresponding coumarinic acid (XIII) can also be isolated from this substance, although it passes slowly into the coumarin on keeping at the ordinary temperature:





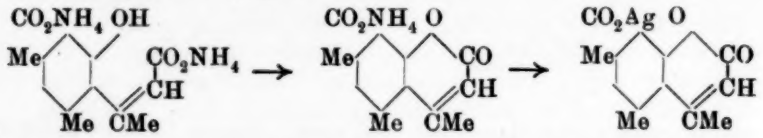
(XIII.)

It is evident that during the hydrolysis of the fully-substituted coumarin (IV) by sulphuric acid, the carbethoxy-group in position 6 is eliminated as soon as hydrolysed. This is proved by the fact that if the hydrolysis is stopped before completion a compound is formed (XIV), which contains a free carboxyl group in position 8:

(XIV.)

This coumarinic acid possesses remarkable stability; in fact, the corresponding coumarin cannot be obtained from it, since it passes at its melting point (300°), with loss of carbon dioxide, into 4 : 5 : 7-trimethylcoumarin. As a matter of fact, the reactions of this carboxylic acid illustrate in a marked degree the curious properties which are conferred on a derivative of coumarin having a carboxyl group in the position 8. Moreover, it is evident that the stability of the coumarinic acid is not determined by the weight of the group in this position, but entirely by its acidic properties. This is shown by the fact that although the substance behaves on titration as a dibasic acid, a neutral solution of the diammonium salt, when boiled, eliminates ammonia and passes

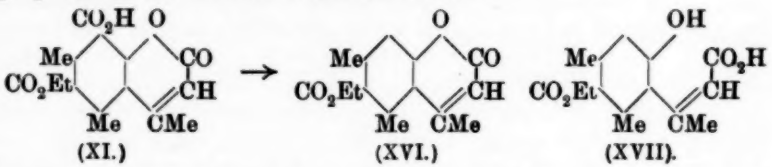
into the ammonium salt of the coumarin, from which the silver salt is precipitated by silver nitrate:



In the same way, when the acid is esterified through the silver salt, the stable form of the ester (XV) is the coumarin, and not the coumarinic acid. The proof that the carboxyl group in this compound is in the position 8 is supplied by the fact that it can be esterified through the silver salt, and the ester (XV) so formed is so readily hydrolysed by alkali that the alkali salt of the acid is produced before the coumarin ring is broken, and hence it is not possible to isolate the coumarinic acid corresponding with the ester:

(XV.)

Moreover, the coumarin ester (XVI) can be prepared from the acid (XI), and it is a different substance from the isomeric ester prepared in the manner described above:



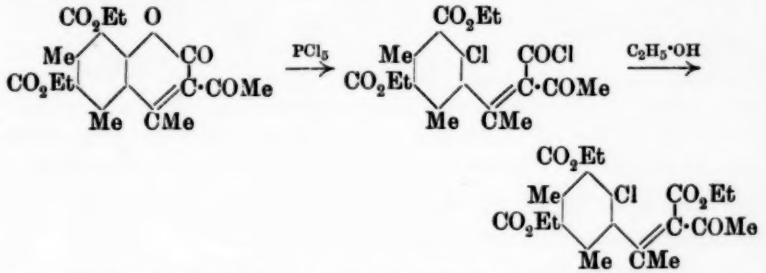
(XI.) (XVI.) (XVII.)

The ester (XVI) is converted into the salt of the coumarinic acid (XVII) by alkali, but prolonged treatment has no effect on the carbethoxy-group.

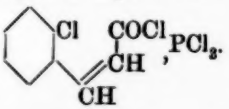
The relative stability of the two carboxylic acids (XI) and (XIV) is worthy of note. The former (XI) does not lose carbon dioxide on being heated, but passes into the coumarin; carbon dioxide is evolved only when the substance is heated with water at a high temperature. On the other hand, the acid (XIV) loses carbon dioxide at the melting point. The only explanation of these facts must be based on the assumption that the coumarin ring is more readily formed from the compound of formula (XI) than from the substance which has no substituting group in the position 6.

The stability of the coumarinic acids as shown by the examples

quoted above gave rise to the suggestion that in all probability it would be possible to prepare chlorine derivatives by the action of phosphorus pentachloride, a reaction which has not been observed hitherto in the case of coumarin or its derivatives. The reaction was found to proceed in the expected manner so far as the end-products were concerned; for example, the substance melting at 135° was found to react quantitatively in accordance with the scheme:



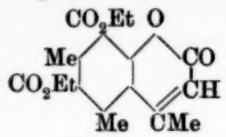
However, in the course of the reaction a quite unexpected effect was obtained, for it was found that the action of phosphorus pentachloride and phosphoryl chloride produced an intense purple solution, the colour of which disappeared when poured into alcohol. An examination of several coumarin derivatives which had been prepared by Mr. B. B. Dey, of this College, showed this reaction to be common to all coumarins which had a substituting group in position 4. All other coumarins failed to give colours, but gave, instead, crystalline precipitates, which, in the case of coumarin itself, appeared to be an additive product of phosphorus trichloride with the chloro-acid chloride of the coumarinic acid, having a structure represented by the expression



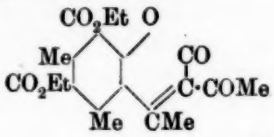
The highly-coloured products from the 4-methylcoumarins can be isolated as dark blue powders with a coppery reflex. They contain phosphorus, and are rapidly acted on by moist air. Their halogen content points to a formula similar to that assigned to the compound from coumarin itself, a view which is supported by the fact that when treated with water they yield either the coumarin or coumarinic acid. It is intended to study this reaction more completely in the near future.

The well-known reaction by which coumarin absorbs two atoms of bromine by the action of the halogen in carbon disulphide is exhibited by the substituted coumarins described in this paper.

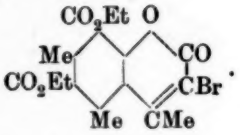
Two atomic proportions of bromine are absorbed, but hydrogen bromide is at once eliminated, and a compound containing bromine, in the usual position 3, is formed. If this position is occupied by an acetyl group, this is eliminated, and bromine takes its place. Thus the two compounds:



and



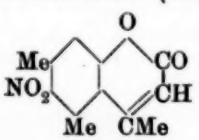
give



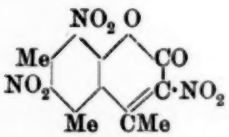
The action of alkali on this bromocoumarin produces the corresponding coumarilic acid, thus:

and it is interesting to note that these compounds do not give colorations with phosphorus pentachloride.

The nitration of coumarins and alkylcoumarins has been investigated by Clayton (T., 1910, **97**, 1396); the results which we have obtained by nitrating the coumarins described in this communication may be summarised briefly as follows. The nitration of 4 : 5 : 7-trimethylcoumarin leads, in the first instance, to the formation of the 6-nitro-derivative (XVIII), and further nitration yields the trinitro-derivative (XIX).

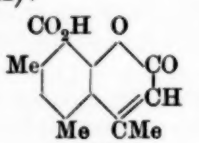


(XVIII.)

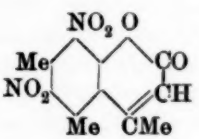


(XIX.)

The intermediate dinitro-derivative (XX) could not be isolated in this reaction, but it is readily formed by the nitration of the acid (XXI):



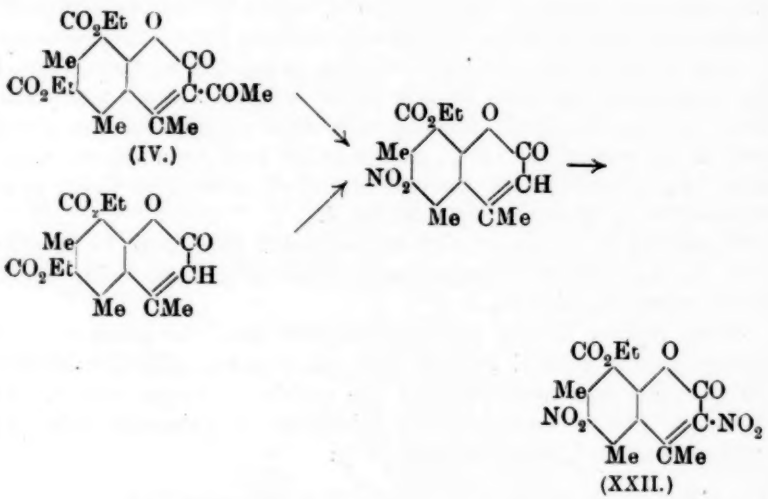
(XXI.)



(XX.)

Attention was drawn by Clayton (*loc. cit.*) to the stability of the coumarinic acid derived from nitrocoumarins having the nitro-group in the position 8. This statement is supported by the behaviour of the nitro-coumarins described above, for whereas the coumarinic acid from the 6-nitro-derivative cannot be isolated, the 6 : 8-dinitro-derivative yields a stable coumarinic acid. The trinitro-derivative gives ω : 3 : 5-trinitro-2-hydroxy-α : 4 : 6-trimethylstyrene when treated with alkali.

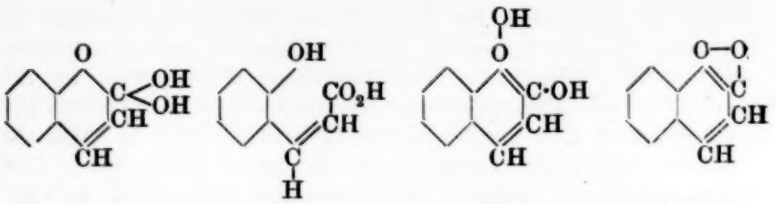
The ease with which the nitro-group enters the position 6, and the difficulty with which it is introduced into the position 3, is illustrated by the nitration of the fully-substituted coumarin (IV). The nitration of this substance causes the elimination of the acetyl group without introducing a nitro-group in its place, but, at the same time, the carbethoxy-group in position 6 is displaced by a nitro-group. The same nitro-derivative is also formed from the coumarin less the acetyl group:



Prolonged nitration leads to the formation of the 3 : 6-dinitro-derivative (XXII) without affecting the carbethoxy-group in position 8.

The Constitution of Coumarinic Acid.

Coumarin, when dissolved in aqueous sodium hydroxide, yields a yellow solution of the sodium salt of coumarinic acid, from which acids re-precipitate the original coumarin. The formulæ which have been proposed for this acid may be summarised as follows:



(I.) (II.) (III.) (IV.)

Formula I was proposed by Michael (*J. pr. Chem.*, 1888, [ii], **38**, 27); it was shown to be improbable by the experiments of Clayton (T., 1910, **97**, 2102). Formula II is the ordinary *cis*-formula for the acid; whilst explaining the general properties of the acid, this structure fails to account for the yellow colour of the sodium salt. Formula III is suggested by Clayton (*loc. cit.*) as corresponding with the formula for coumarin (IV) proposed by Morgan and Micklethwait (T., 1906, **89**, 868). Apart from the question as to the peroxide formula for coumarin, there is no experimental evidence whatever which favours this formula for coumarinic acid.

One of the most striking facts that arises out of the study of the coumarins described in this paper is that, without exception, they dissolve in alkali, forming colourless solution of the alkali salt of the coumarinic acid. So far as we have been able to ascertain, this appears to be characteristic of all coumarins which have a substituting group in the position 4.

It follows, therefore, that these coumarinic acids must be in some way fundamentally different from those coumarinic acids which form yellow alkali salts.

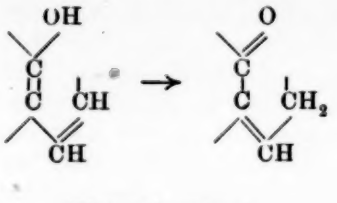
Now, it is a fact of some significance that the presence of a group on the central carbon atom of a system C:C·CH hinders or prevents the movement of the mobile hydrogen within the system. This is shown by the behaviour of glutaconic acid (V) and of β-methylglutaconic acid (VI):

$CO_2H\cdot\dot{C}H\cdot CH_2\cdot\dot{C}H\cdot CO_2H$ (V.)

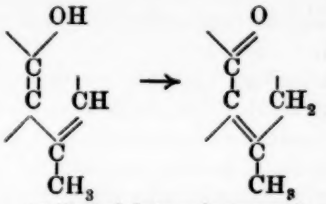
$CO_2H\cdot\dot{C}H\cdot CHMe\cdot CH\cdot CO_2H$ (VI.)

$CO_2H\cdot CH{:}CMe\cdot CH_2\cdot CO_2H$ (VII.)

for whereas the former can only be isolated in one modification, the latter can be readily converted into its isomeride (VII) (T., 1912, **101**, 856). An analysis of the formulæ of coumarinic acid and of the 4-substituted coumarinic acids shows that these systems are present, thus:

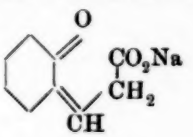


(Glutaconic system.)

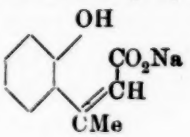


(β-Methylglutaconic system.)

and that, apart from any question as to the structure of the glutaconic portion of the molecule, it is to be expected that the transference of the hydroxylic hydrogen to the terminal carbon atom of the conjugated system would take place with greater readiness in the coumarinic molecule than in the molecule in which the 4-carbon atom is substituted by methyl. This leads to the conclusion that the salts of coumarinic acid are *o*-quinone derivatives (VIII), whereas the corresponding salts of the 4-substituted acids have the normal coumarinic acid structure (IX):



(VIII.)

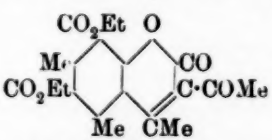


(IX.)

They are, therefore, in the one case yellow, and in the other colourless. Experiments are now in progress which it is hoped will throw further light on this question.

Experimental.

Ethyl 3-Acetyl-4 : 5 : 7-trimethylcoumarin-6 : 8-dicarboxylate,



This substance was originally prepared as a by-product in the formation of ethyl β-methylglutaconate from ethyl *iso*dehydracetate by the action of cold alcoholic sodium ethoxide, and the details of the process have been given previously (T., 1912, **101**, 1565). The conditions stated below were ultimately found to give a yield of 30 per cent. of this coumarin derivative. Twenty-three grams of sodium, dissolved in 270 grams of alcohol, were added to 100 grams of ethyl *iso*dehydracetate, and the mixture was kept below 0° by means of ice and salt. After three hours, water was added, and the labile ester of β-methylglutaconic acid extracted by ether.

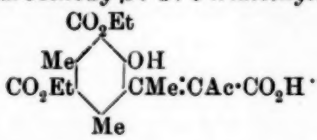
The aqueous solution was then acidified and extracted by the ether, the residual oil, left after evaporating the ether, being then esterified by alcohol and sulphuric acid in the usual manner. The neutral oil obtained in this way was then fractionated under diminished pressure, and was thus separated into two fractions, the one boiling at 167°/68 mm., and consisting of ethyl β-methylglutaconate, the other boiling at 253°/18 mm. The fraction of higher boiling point became solid on keeping, and when recrystallised from alcohol yielded well-defined needles, which melted at 135°:

0·1532 gave 0·3613 CO_2 and 0·0825 H_2O. C = 64·31; H = 5·98.
$C_{20}H_{22}O_7$ requires C = 64·2; H = 5·9 per cent.

The acetyl group was estimated by Perkin's method: $CO{\cdot}CH_3$ = 11·24. $C_{18}H_{19}O_6{\cdot}CO{\cdot}CH_3$ requires $CO{\cdot}CH_3$ = 11·51 per cent.

The coumarin is characterised by being very sparingly soluble in ether; it gives no coloration with ferric chloride in alcoholic solution.

α-Acetyl-3: 5-dicarbethoxy-β: 4: 6-trimethylcoumarinic Acid,

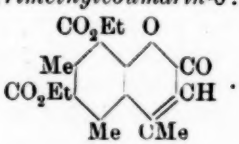


The coumarin, melting at 135°, dissolves when warmed with concentrated aqueous alkali hydroxide, and the above *acid* is precipitated when the solution is acidified. It separates from dilute alcohol as small plates, which melt at 146° and eliminate water vapour at 150°:

0·1586 gave 0·3545 CO_2 and 0·0915 H_2O. C = 60·98; H = 6·41.
$C_{20}H_{24}O_8$ requires C = 61·2; H = 6·1 per cent.

The acid is converted completely into the coumarin when heated above its melting point, but can be recrystallised without losing water. An alcoholic solution gives a deep purple colour with ferric chloride.

Ethyl 4: 5: 7-*Trimethylcoumarin*-6: 8-*dicarboxylate*,



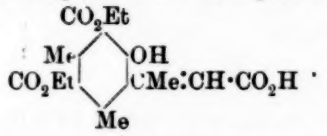
This substance was prepared from the acetyl derivative, melting at 135°, by means of alcohol and sulphuric acid in the manner

described by A. G. Perkin (T., 1905, **87**, 109) for the elimination of acetyl groups. It crystallises from alcohol in concentric needles, which melt at 131°:

0·1892 gave 0·4496 CO_2 and 0·1009 H_2O. C = 64·78; H = 5·92.
$C_{18}H_{20}O_6$ requires C = 65·1; H = 6·0 per cent.

The coumarin is insoluble in cold aqueous alkalis.

3 : 5-*Dicarbethoxy*-β : 4 : 6-*trimethylcoumarinic Acid*,

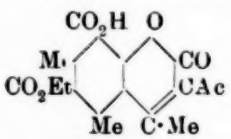


Dilute aqueous potassium hydroxide dissolves the coumarin, melting at 131°, when warmed, and the *coumarinic acid* is precipitated from the solution by the addition of mineral acids. It crystallises from dilute alcohol in glistening plates, which melt at 122°:

0·1245 gave 0·2799 CO_2 and 0·0726 H_2O. C = 61·32; H = 6·48.
$C_{18}H_{22}O_7$ requires C = 61·7; H = 6·3 per cent.

The acid gives a deep purple colour with ferric chloride, and when heated at 150° loses water and passes into the coumarin, melting at 131°.

6-*Ethyl* 8-*Hydrogen* 3-*Acetyl*-4 : 5 : 7-*trimethylcoumarin*-6 : 8-*dicarboxylate* and α-*Acetyl*-3-*carboxy*-5-*carbethoxy*-β : 4 : 6-*trimethylcoumarinic Acid*,



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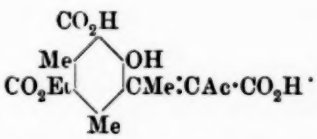


The *sodium* salt of the coumarinic acid is formed when the coumarin, melting at 135°, is boiled for several hours with 50 per cent. aqueous sodium hydroxide, and the *acid* is precipitated when the solution is cautiously acidified. It crystallises from dilute alcohol in small plates, which melt at 176°:

0·1999 gave 0·4373 CO_2 and 0·1012 H_2O. C = 59·51; H = 5·63.
$C_{18}H_{20}O_8$ requires C = 59·3; H = 5·5 per cent.

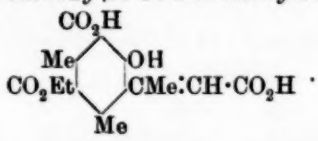
The acid, which gives a purple colour with ferric chloride, evolves water vapour when heated a few degrees above its melting point, and passes into the *coumarin*. This substance crystallises from alcohol as small needles, which melt at 235°:

0·2268 gave 0·5238 CO_2 and 0·1097 H_2O. C = 63·12; H = 5·38.
$C_{18}H_{18}O_7$ requires C = 62·4; H = 5·2 per cent.

The coumarin is reconverted into the sodium salt of the coumarinic acid by warm aqueous sodium hydroxide.

An estimation of the acetyl group gave $CO{\cdot}CH_3 = 12{\cdot}80$. $C_{16}H_{15}O_6{\cdot}CO{\cdot}CH_3$ requires $CO{\cdot}CH_3 = 12{\cdot}43$ per cent.

3-Carboxy-5-carbethoxy-β: 4: 6-trimethylcoumarinic Acid,

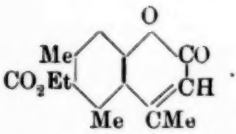


It is remarkable that the elimination of the acetyl group from either the coumarin or coumarinic acid last mentioned should lead in each instance to the formation of the above *coumarinic acid*. The process was carried out in the usual way, and the product recrystallised from dilute alcohol, from which solvent it separated in white needles, which melted at 129°:

0·1774 gave 0·1952 CO_2 and 0·0892 H_2O. C = 59·98; H = 5·59.
$C_{16}H_{18}O_7$ requires C = 59·6; H = 5·6 per cent.

The compound gives a deep purple colour with ferric chloride, and does not evolve water when heated. We have, therefore, been unable to prepare the corresponding coumarin from it, and the remarkable stability of this acid compared with that of the other compounds of similar type serves as another example of the effect produced by the carboxyl group in position 8.

6-Carbethoxy-4: 5: 7-trimethylcoumarin,



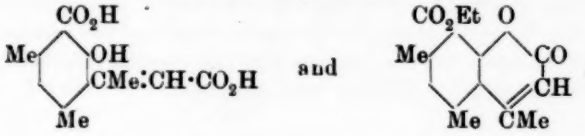
Although the coumarinic acid described in the last paragraph evolves carbon dioxide when heated at a high temperature, much decomposition and charring also occurs, and no definite product could be isolated. If, however, the acid is heated in a sealed tube with water at 180° for five hours, the above *coumarin* is formed in almost quantitative yield. It crystallises from alcohol in clusters of small needles, melting at 124°:

0·1419 gave 0·3586 CO_2 and 0·0778 H_2O. C = 68·91; H = 6·09.
$C_{15}H_{16}O_4$ requires C = 69·2; H = 6·1 per cent.

The coumarin dissolves when warmed with dilute aqueous alkali, but is re-precipitated when the solution is acidified. It is evident, therefore, that the coumarinic acid passes at once into the coumarin when liberated from its salts. Prolonged boiling with 50 per cent.

aqueous alkali hydroxide fails to cause hydrolysis of the ester grouping.

3-Carboxy-β: 4: 6-trimethylcoumarinic Acid and 8-Carbethoxy-4: 5: 7-trimethylcoumarin,



The *coumarinic acid* accompanies 4:5:7-trimethylcoumarin when the hydrolysis of the fully-substituted coumarin, melting at 135° (see p. 397), is carried out by means of 50 per cent. aqueous sulphuric acid. The amount formed depends entirely on the length of time during which the liquid is boiled. As a rule, 25 grams of the coumarin mixed with 200 c.c. of the mineral acid gave about equal proportions of the carboxylic acid and 4: 5: 7-trimethylcoumarin after being boiled for two hours. The two products, which crystallise from the clear solution on cooling, can be separated by means of dilute aqueous sodium carbonate.

The acid dissolves in hot water, but is best recrystallised from dilute alcohol, from which it separates in slender needles, melting at 300°, with evolution of carbon dioxide:

0·1946 gave 0·4457 CO_2 and 0·0988 H_2O. C = 62·46; H = 5·64.

$C_{13}H_{14}O_5$ requires C = 62·4; H = 5·6 per cent.

The acid gives a violet colour with ferric chloride, and is dibasic:

0·9654 required 38·7 c.c. *N*/5-NaOH.

$C_{13}H_{14}O_5$ (dibasic) requires 38·6 c.c.

The acid cannot be converted into the corresponding coumarin, since on being heated above its melting point it loses carbon dioxide and passes into 4: 5: 7-trimethylcoumarin.

Ethyl Ester.—It is a remarkable fact that although the coumarinic acid titrates as a dibasic acid and exhibits such exceptional stability when the carboxyl group is free, the neutral solution of the diammonium salt, when boiled, eliminates ammonia, and the *silver* salt precipitated from the neutral solution is the salt of the coumarin:

0·1492 gave 0·0476 Ag. Ag = 31·89.

$C_{13}H_{11}O_4Ag$ requires Ag = 31·9 per cent.

When the acid is regenerated, either from the silver salt or from the corresponding ammonium salt, it is the coumarinic acid, melting at 300°, that is obtained, and not the coumarin.

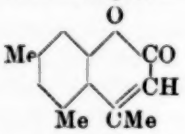
The dried silver salt is readily transformed into the *ethyl* ester

when treated with ethyl iodide in dry ether. It crystallises from dilute alcohol in brilliant, colourless laminæ, which melt at 133°:

0·1289 gave 0·3271 CO_2 and 0·0692 H_2O. C = 69·21; H = 5·96.
$C_{15}H_{16}O_4$ requires C = 69·2; H = 6·1 per cent.

The ester is insoluble in cold aqueous sodium hydroxide, but dissolves on warming. During this process it is evident that the ester group is hydrolysed at the same time as the coumarin ring is broken, because the acid formed is the coumarinic acid, melting at 300°, from which the ester was derived.

4 : 5 : 7-*Trimethylcoumarin and* β : 4 : 6-*Trimethylcoumarinic Acid*,



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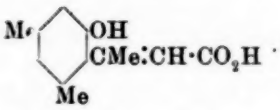


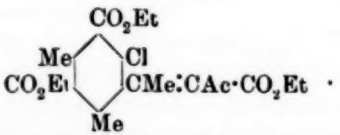
The *coumarin* accompanies the carboxylic acid in the experiment described above, and can be isolated, owing to its insolubility in cold aqueous sodium carbonate. It is the sole product if the hydrolysis is continued for four hours. It crystallises from alcohol in lustrous laminæ, which melt at 178°. (Found, C = 76·56; H = 6·40. $C_{12}H_{12}O_2$ requires C = 76·6; H = 6·4 per cent.) The identity of this substance with the coumarin prepared by Clayton (T., 1908, **93**, 2020) was established by direct comparison.

The coumarin dissolves in warm aqueous alkali hydroxide, and if the solution is carefully acidified at 0°, the *coumarinic acid* separates in small needles, which melt at 128°, with evolution of water vapour:

0·1312 gave 0·3353 CO_2 and 0·0797 H_2O. C = 69·70; H = 6·91.
$C_{12}H_{14}O_3$ requires C = 69·9; H = 6·8 per cent.

The acid, which gives a deep blue colour with ferric chloride, is very unstable, and is completely converted into the coumarin on keeping at the ordinary temperature. When it is boiled with water, the conversion is very rapid. It could not be recrystallised.

Ethyl 2-*Chloro*-α-*acetyl*-3 : 5-*dicarbethoxy*-β : 4 : 6-*trimethylcinnamate*,



The action of an equivalent amount of phosphorus pentachloride on the fully-substituted coumarin, melting at 135° (see p. 397),

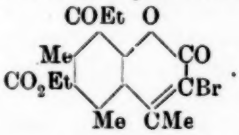
dissolved in hot phosphoryl chloride, leads, in the first instance, to the production of a deep purple solution, from which dry ether precipitates a blue solid with a marked coppery reflex. This compound, which is very unstable, and quickly absorbs moisture from the air, contains phosphorus, and is evidently a compound of the chloro-acid chloride with phosphorus trichloride, since, when it is treated with alcohol, the colour is discharged, and the addition of water precipitates the above *chloro-ester*. The ester is obtained as a yellow oil by extraction with ether; it cannot be distilled without undergoing decomposition:

0·5081 gave 0·1700 AgCl. Cl = 8·27.

$C_{22}H_{27}O_7Cl$ requires Cl = 8·1 per cent.

The action of alkaline hydrolysing agents converts the chloro-ester into the coumarinic acid, melting at 146°, corresponding with the coumarin from which the chloro-derivative was obtained.

Ethyl 3-*Bromo*-4 : 5 : 7-*trimethylcoumarin*-6 : 8-*dicarboxylate*,



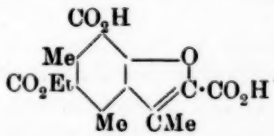
The action of bromine dissolved in chloroform on the fully-substituted coumarin, melting at 135°, produces the same compound as that formed from the deacetylated compound melting at 131° (see p. 398), and it is evident, therefore, that the bromine displaces the acetyl group in the position 3. It is necessary to boil the chloroform solution containing the coumarin and the requisite amount of bromine until the elimination of hydrogen bromide has ceased, when the product can be isolated by evaporation, and purified by recrystallisation from alcohol. It forms small needles, which melt at 114°:

0·1732 gave 0·3325 CO_2 and 0·0750 H_2O. C = 52·32; H = 4·81.

0·2780 „ 0·1280 AgBr. Br = 19·59.

$C_{18}H_{19}O_6Br$ requires C = 52·5; H = 4·6; Br = 19·5 per cent.

4-*Carbethoxy*-6-*carboxy*-2 : 3 : 5-*trimethylcoumarilic Acid*,



This substance was obtained from the above coumarin by boiling it with an excess of potassium hydroxide dissolved in alcohol for

two hours. The product, isolated in the usual way, crystallises from dilute alcohol in colourless flakes, which melt at 197°:

0·1651 gave 0·3624 CO_2 and 0·0774 H_2O. C = 59·85; H = 5·21.

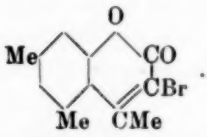
$C_{16}H_{16}O_7$ requires C = 60·0; H = 5·0 per cent.

An analysis of the *silver* salt gave the following figures:

0·1977 gave 0·0793 Ag. Ag = 40·12.

$C_{16}H_{14}O_7Ag_2$ requires Ag = 40·5 per cent.

3-Bromo-4 : 5 : 7-trimethylcoumarin,



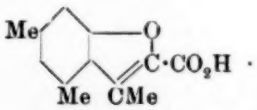
Both 4 : 5 : 7-trimethylcoumarin and the corresponding coumarinic acid readily absorb bromine from its solution in chloroform in the cold. The product obtained by evaporating the solvent crystallises from alcohol in small plates, which melt at 163°:

0·1508 gave 0·1064 AgBr. Br = 30·02.

$C_{12}H_{11}O_2Br$ requires Br = 30·0 per cent.

The compound is insoluble in alkali.

2 : 3 : 5-Trimethylcoumarilic Acid,



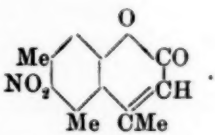
This substance is formed from the last-mentioned coumarin by boiling it with dilute aqueous potassium hydroxide until dissolved. It separates when the alkaline solution is acidified, and can be obtained as a white, crystalline solid by recrystallisation from alcohol. It melts at 149°.

The following analysis of the silver salt was made:

0·1641 gave 0·0570 Ag. Ag = 34·73.

$C_{12}H_{11}O_3Ag$ requires Ag = 34·7 per cent.

6-Nitro-4 : 5 : 7-trimethylcoumarin,



This substance is produced by the nitration of 4 : 5 : 7-trimethylcoumarin under the following conditions. One gram of the coumarin is dissolved in 10 c.c. of concentrated sulphuric acid, and 2 c.c. of a nitrating mixture, composed of one part of nitric acid to three parts of sulphuric acid, are added, the mixture being kept below 0°. After being kept at the ordinary temperature for thirty

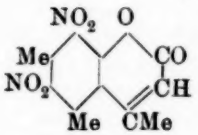
minutes, the liquid is poured on ice, and the solid separated. It crystallises from glacial acetic acid in colourless needles, which melt at 208°:

0·1646 gave 8·7 c.c. N_2 at 20° and 756 mm. N = 6·01.

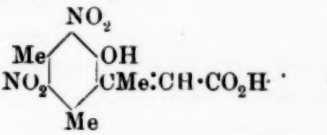
$C_{12}H_{11}O_4N$ requires N = 6·0 per cent.

The nitro-compound is insoluble in cold aqueous alkali hydroxide, but on boiling it dissolves, and the solution becomes deep orange-red. The careful addition of mineral acid to this solution causes the precipitation of the original coumarin. It is therefore evident that the coumarinic acid is not sufficiently stable to be isolated.

6 : 8-*Dinitro*-4 : 5 : 7-*trimethylcoumarin and* 3 : 5-*Dinitro*-β : 4 : 6-*trimethylcoumarinic Acid*,



and



In order to prepare the *coumarin*, 3 grams of the 8-carboxylic acid, melting at 300° (see p. 401), were added to 25 c.c. of boiling solution containing equal quantities of concentrated nitric acid and water. The clear solution deposited the dinitro-compound on cooling, and it was purified by recrystallisation from absolute alcohol. It forms colourless needles, which melt at 203°:

0·1115 gave 10·1 c.c. N_2 at 20° and 756 mm. N = 10·31.

$C_{12}H_{10}O_6N_2$ requires N = 10·1 per cent.

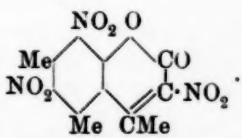
The coumarin gradually forms an orange-red solution when it is boiled with aqueous alkali hydroxide, and if this solution is cautiously acidified, a yellow, crystalline precipitate of the *coumarinic acid* is deposited. The acid cannot be recrystallised without change, but can be purified by rubbing with dry ether. It melts and decomposes vigorously at 182°:

0·2127 gave 18·4 c.c. N_2 at 21° and 750 mm. N = 9·71.

$C_{12}H_{12}O_7N_2$ requires N = 9·5 per cent.

The acid changes to the coumarin on keeping at the ordinary temperature, and the conversion is rapid if it is boiled with water.

3 : 6 : 8-*Trinitro*-4 : 5 : 7-*trimethylcoumarin*,



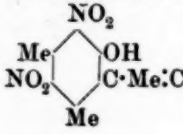
This substance can be prepared by dissolving 2 grams of trimethylcoumarin in 15 c.c. of concentrated sulphuric acid, adding

15 c.c. of the nitrating mixture, prepared as in the first experiment, and pouring on ice after keeping at the ordinary temperature for twelve hours. A solid separates, which crystallises from glacial acetic acid in cream-coloured, flattened needles, which melt at 225°:

0·1571 gave 19·1 c.c. N_2 at 24·5° and 753 mm. N = 13·32.

$C_{12}H_9O_8N_3$ requires N = 13·0 per cent.

ω : 3 : 5-*Trinitro*-2-*hydroxy*-α : 4 : 6-*trimethylstyrene*,

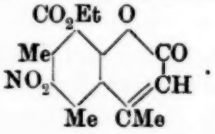


This substance was prepared by the action of alkali on the trinitro-derivative in the manner described by Clayton. The product is difficult to obtain pure, but this can be effected by repeated recrystallisation from benzene. It forms crystalline nodules, which melt at 103°:

0·1454 gave 17·8 c.c. N_2 at 21·5° and 756 mm. N = 13·85.

$C_{11}H_{11}O_7N_3$ requires N = 14·1 per cent.

Ethyl 6-*Nitro*-4 : 5 : 7-*trimethylcoumarin*-8-*carboxylate*,



This nitro-compound can be prepared either from the fully-substituted coumarin, melting at 135°, or from the deacetylated product, melting at 131°. One gram of either of these compounds is dissolved in 10 c.c. of concentrated sulphuric acid, and treated with 2 c.c. of the nitrating mixture at 0°. After being kept at room temperature for thirty minutes, the clear liquid is poured on ice, and the solid separated. It crystallises from glacial acetic acid in colourless needles, which melt at 170°:

0·2139 gave 9·2 c.c. N_2 at 21° and 756 mm. N = 4·87.

$C_{15}H_{15}O_6N$ requires N = 4·6 per cent.

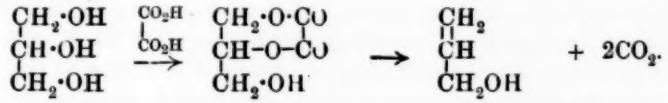
The coumarin dissolves when boiled with aqueous alkali, forming a deep yellow solution, but the addition of acids causes the coumarin to be re-precipitated.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received March 4th*, 1915.]

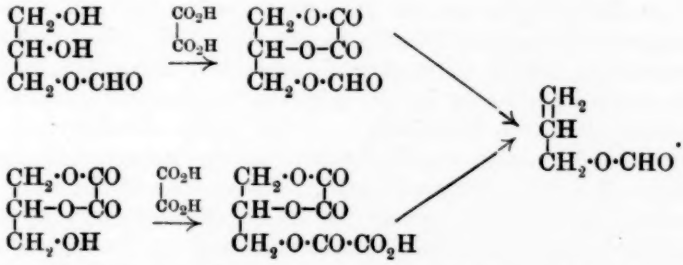
XLVII.—*The Preparation of Allyl Alcohol.*

By Frederick Daniel Chattaway.

Allyl alcohol was first prepared from allyl iodide. This, however, since it had to be made from glycerol, was usually mixed with *iso*propyl iodide, from which it could be separated only with difficulty. The various procedures adopted to replace the iodine by hydroxyl were, moreover, somewhat complicated, and the yields consequently poor. These older methods were therefore at once abandoned when Tollens discovered that allyl alcohol could be obtained directly from glycerol by heating it with oxalic acid. It has recently been shown (T., 1914, **105**, 151) that allyl alcohol is produced in this reaction by the decomposition at a high temperature of the normal oxalic ester of glycerol, namely, dioxalin, which is one of the first products of the interaction of oxalic acid and glycerol:



Allyl formate, which is always obtained together with the allyl alcohol and gives to the crude product its extraordinarily irritant quality, results from a similar decomposition of monoformin-dioxalin, which may be produced either from monoformin by the further action of oxalic acid or from dioxalin by the formation and decomposition of an acid oxalate, both actions probably occurring:



This elucidation of the course of the reaction shows that the most favourable conditions for the production of allyl alcohol are those which promote the formation of the normal dioxalins, and that any are disadvantageous which tend to their hydrolysis. It is best, therefore, to work with anhydrous materials, as thereby the

dioxalins are formed in the largest possible amount, and the production of the acid oxalate, which, by its decomposition, yields monoformin, is as far as possible prevented.

It is advantageous also to use a considerable excess of oxalic acid, the allyl formate, which is in consequence obtained in larger amount, being easily hydrolysed to the alcohol if not required.

The following procedure has been found most speedy and advantageous. It gives a theoretical yield of allyl alcohol from the glycerol actually reacting, and even when the amount of oxalic acid used is considered gives a yield twice as great as the best that can be obtained by Tollens and Henninger's familiar method.

Five hundred grams of anhydrous oxalic acid are added to 500 grams of glycerol in a 1·5 litre flask, and the mixture is heated on a water-bath in the partial vacuum produced by a good water-pump until formic acid ceases to distil over. Four or five hours is generally sufficient, although the heating may with advantage be prolonged for several additional hours. No frothing takes place, and the process requires little attention. When once begun, the heating should not be interrupted, as on cooling the mass becomes much more viscid, and being saturated with carbon dioxide frothing generally occurs on resuming the heating. This, however, is not serious, and by disconnecting the pump from time to time the liquid can be prevented from passing over into the receiver.

When nothing further distils over in the partial vacuum at 100°, the mixture is heated very slowly under the ordinary pressure over a wire gauze with a thermometer immersed in the liquid until the temperature reaches 240°. If the preliminary heating has been continued sufficiently long, only 5—6 c.c. should distil over before a temperature of 210° is reached; whatever passes over, however, may be rejected, as it is mainly water and formic acid.

When the temperature of the liquid reaches 220—225° rapid disengagement of carbon dioxide occurs, and allyl alcohol and allyl formate distil over in approximately equal amounts. The bulk of the decomposition occurs in the neighbourhood of 223°, and when 230° is reached it is practically complete. The reaction is at an end when liquid ceases to distil over, but the temperature should never be allowed to rise above 240°. The residue in the flask can then be made up to 500 grams by the addition of more glycerol, a further 500 grams of anhydrous oxalic acid can be added, and the process repeated. When this has been done four or five times it is best not to use the residue further, as it shows a tendency to froth during the preliminary heating.

If the final heating is carefully conducted and the temperature not allowed to rise above 235—240°, practically no acrolein is

produced, and the residue, consisting mainly of glycerol, is only slightly discoloured.

Owing to the extremely acrid nature of the volatile allyl formate, some of the vapour of which is carried through the condenser by the escaping carbon dioxide, it is best to pass the issuing gas through a small flask filled with lumps of ice, and then conduct it into a draught chamber or into the outer air. A small loss of allyl formate, which is condensed by the ice, is also thus prevented.

It is advisable when heating under the ordinary pressure to fit the flask with a short fractionating column, as otherwise some 30—40 grams of glycerol distil over and are lost. The exact amount thus distilling over depends on the rate at which the decomposition is effected. By using a column most of this glycerol, which would otherwise be wasted, is condensed, and returned to the distilling flask. A Young column with four pear-shaped bulbs is a suitable one to use.

In order to obtain allyl alcohol there is added to the liquid which distils over while the temperature rises from 210° to 235° a solution of 50 grams of sodium hydroxide in a litre of water, and the mixture is kept at the ordinary temperature for twelve hours or thereabouts in order to hydrolyse the allyl formate. The liquid is then distilled, and the first 300 c.c. passing over, which contain the whole of the allyl alcohol, are collected. By fractionating this distillate, the allyl alcohol can easily be obtained as a constant boiling mixture with water. This boils at 87—88° under the ordinary pressure, contains from 27 to 28 per cent. of water, and can be used for most purposes for which allyl alcohol is required. In this separation a fractionating column is necessary. A Young column with twelve pear-shaped bulbs answers the purpose well.

If such a column is not available a similar mixture of water and allyl alcohol can be separated from the 300 c.c. of distillate, as a lighter layer which floats on the surface, by adding 50 grams of anhydrous potassium carbonate.

If the allyl alcohol is required free from water the constant boiling mixture can be further dehydrated by adding from time to time small quantities of anhydrous potassium carbonate—about 10 grams is a convenient quantity to use—and discarding the heavy aqueous layer as long as one separates. When this no longer happens and the potassium carbonate remains solid after some hours, the allyl alcohol is filtered off and distilled, all that passes over below 96° being collected apart and re-dehydrated by potassium carbonate.

The remaining portion—generally more than half of the whole—

distils between 96° and 97°, and is practically pure allyl alcohol.

If the isolation of the allyl formate, present to the extent, roughly, of 50 per cent. in the original product of heating, be desired, it is best to distil this directly, using the twelve-bulb fractionating column, collecting apart all passing over below 87°. This, when washed a few times with a very little water to remove allyl alcohol, and dried over fused calcium chloride, gives on distillation pure allyl formate boiling at 82—83° under the ordinary pressure.

It is generally possible, using 500 grams of glycerol and 500 grams of anhydrous oxalic acid, to obtain in one operation about 200 to 210 grams of the constant boiling mixture of allyl alcohol and water, or about 150 grams of pure allyl alcohol.

If the crude distillate from similar quantities is fractionated to obtain the allyl formate about 90 grams of the pure ester can generally be obtained.

The weight of the residue left after the decomposition of the dioxalin is usually somewhat less than half that of the glycerol used.

The yield of allyl alcohol in a carefully conducted experiment in which all the residues are worked up is practically theoretical, calculated on the amount of glycerol actually used up.

The distillate passing over during the preliminary heating on the water-bath in a vacuum contains a considerable quantity of formic acid, and can be used for the preparation of the salts of this acid.

The addition of a small quantity of ammonium chloride recommended by Tollens has not been found to be of any advantage; the yield of allyl alcohol, when the ordinary glycerol and oxalic acid of commerce are employed, is not thereby increased, whilst the glycerol left after the heating is considerably discoloured and rendered less suitable for repeated use.

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[*Received Feb.* 18*th*, 1915].

XLVIII.—*Blue Adsorption Compounds of Iodine. Parts II and III. Derivatives of α- and of γ-Pyrone.*

By George Barger and Walter William Starling.

It will be shown in this paper that, in addition to starch, cholalic acid, saponarin and a few other natural substances (Barger and Field, T., 1912, **101**, 1394), a large number of synthetic compounds give blue additive products with iodine, and that there is a connexion between the power of taking up iodine and the chemical constitution. The additive products are either mixed crystals (solid solutions) or so-called adsorption compounds, in which case the adsorbent is the organic substance in an amorphous state or in colloidal solution. We are therefore, for the first time, able to trace the effect of constitution on adsorptive power. In previous investigations the constitution of the adsorbed substance only was known, that of the adsorbent (for example, charcoal, in the experiments of Freundlich, "Kapillarchemie," Leipzig, 1909, p. 145) being unknown.

We were led to an examination of pyrone derivatives by the consideration that of the six or eight substances, previously known to take up iodine in the way described, two, namely, euxanthic acid and saponarin, were both γ-pyrones, and later, without special search, we found two other references in the literature. W. H. Perkin, sen. (T., 1871, **9**, 37) described "metallic-looking needles, apparently consisting of a mixture of iodine and coumarin crystallised together," and Czaikowski, Kostanecki and Tambor (*Ber.*, 1900, **33**, 1991) incidentally mention a greyish-black additive compound of apigenin and iodine. Although we are at present primarily concerned with pyrones, we have also observed the reaction with various quinones, phthaleins and other substances.

Conditions Governing the Formation of Iodine Additive Compounds.

As was shown by Barger and Field (*loc. cit.*), blue compounds are not formed by substances in the molecular disperse condition, or by preformed crystals. Adsorption compounds result only from colloidal solutions or from amorphous gels, and mixed crystals arise only when the substance crystallises in the presence of iodine. Possibly the preformed crystals might also be expected theoretically to take up iodine, but in practice this has not been observed on account of the slow rate of diffusion in solids. Our procedure was

therefore to add a solution of the organic substance in alcohol, or in glacial acetic acid, to a large volume of aqueous potassium triiodide solution, or to dissolve both constituents in alcohol and dilute with water, as recommended by Mylius (*Ber.*, 1887, **20**, 683) for cholalic acid. Substances soluble in alkali may be precipitated more brusquely, with less chance of crystallising, by pouring their alkaline solution into iodine containing excess of acid, but the excess of acid introduces a complication discussed below; the same applies to the use of glacial acetic acid as a solvent.

Substances of small molecular weight often crystallise at once when precipitated from alcoholic solution by aqueous iodine, and if they have not the capacity for forming mixed crystals with iodine, no coloration is observed. If the substance is, however, first precipitated in the amorphous condition, or if a colloidal solution results, iodine may be adsorbed temporarily, and a blue coloration occurs, which may last from a fraction of a second to several days or weeks, depending on the rate of crystallisation. Sometimes, when the organic substance separates from a warm solution in dilute alcohol, containing also iodine, a coloured adsorption compound is obtained on rapid cooling, colourless crystals on slow cooling (compare experimental part, for example, benzo-γ-pyrone-6-methyl-2-carboxylic acid and naphthapyrone). Substances of high molecular weight, for example, α-naphthaflavone, crystallise still more slowly, and yield colloidal solutions, even more sensitive to iodine (1 : 1,000,000) than those of starch. In these cases the coloration is a pure blue, but with some substances at various concentrations of iodine violet, black, purple, pink, or green colorations may be observed. Mixed crystals may be indigo-blue or steel-grey and metallic-looking. The brown adsorption compounds obtained with glycogen and the periodides of alkaloids appear to belong to a different, although closely related, class. Cholalic acid and narceine, for instance, give a blue coloration with dilute, a brown one with more concentrated, iodine solutions.

Amorphous Additive Compounds. Adsorption.

Only a few of the substances under discussion yield colloidal solutions of even moderate stability. Apart from starch, there is saponarin (first wrongly called "soluble starch"), which with iodine furnishes a blue sol of an electronegative lyophobic colloid (Barger and Field, *loc. cit*). A hot saturated solution of euxanthic acid in water also forms an (unstable) sol on cooling, which behaves in the same way to iodine. In all three cases (polysaccharide, glucoside, glucuronic acid) the many hydroxyl groups increase the stability of the colloidal solutions formed. Generally, however, the

organic compound is precipitated by water from alcoholic solution as a gel, in amorphous flakes, which, at the moment of their formation, can take up iodine, but soon lose this property, probably owing to the acquisition of microcrystalline structure. This is, for instance, the case with cholalic acid precipitated from alkaline solution. Basic lanthanum acetate is, however, so thoroughly colloidal that its gel is coloured by iodine even after long keeping.

It is therefore preferable to have the iodine present at the moment of precipitation of the substance. Generally the blue colour appears immediately, but with many substances a delay, of several seconds up to half-an-hour, is observed with dilute iodine solutions (compare, for instance, the behaviour of the benzoyl derivative of 7-hydroxy-4-methylcoumarin, p. 417).

That we are here indeed concerned with adsorption results first, from the distribution of the iodine between solution and gel, according to an exponential formula (demonstrated by Barger and Field in the case of saponarin and cholalic acid), and secondly from the effect of electrolytes on the rate and extent of the adsorption of iodine. Bayliss (*Biochem. J.*, 1906, **1**, 195) has shown that neutral salts increase the adsorption of Congo-red and other negative colloids by filter paper, and further (*Proc. Roy. Soc.*, 1911, [*B*], **84**, 88) that the adsorption of trypsin by a number of adsorbents is increased by calcium sulphate. We have in some cases found very similar effects, that of the cation predominating over that of the anion, as in Bayliss' experiments. The organic substances employed have varying electric charges, mostly negative, and these are neutralised most readily by multivalent cations; thus adsorption of iodine is accelerated by potassium chloride, more so by barium, and still more so by lanthanum chloride (Barger and Field, *loc. cit.*, p. 1402, and euxanthic acid, see below). The opposite inhibitory effect of multivalent anions is not so clear, but 4:3-β-naphthapyrone-2-carboxylic acid and α- and β-naphthaflavones are somewhat less readily coloured by iodine in the presence of sodium phosphate or citrate than in the absence of these salts. With some substances adsorption is greatly favoured by acids; a very small concentration of hydrogen ions may be effective; thus with 5:8-dimethylthioflavone the influence of 0·0001*N*-hydrochloric acid can be detected. In one case only, namely, that of 5-methyl-8-*iso*propylflavone, we observed the opposite effect of hydrogen and multivalent cations, which diminish the adsorption of iodine, here increased by multivalent anions. (The effect of hydroxyl ions could not be investigated in the presence of iodine.) The aberrant behaviour of this substance is probably connected with the high proportion of alkyl groups and its elec-

trical charge. The effect of the concentration of hydrogen ions on adsorption is analogous to the effect on the action of enzymes, for example, pepsin, which action must likewise depend on adsorption, by the substrate.

Crystalline Additive Compounds. Mixed Crystals.

Whereas all the pyrone compounds mentioned in this paper adsorb iodine when they are amorphous, some only are capable of forming mixed crystals with it. In the next section it is shown that the power of adding iodine is closely connected with chemical constitution, but we have not been able to find any connexion between the constitution and the power of forming mixed crystals. Thus in the amorphous state flavone, 6-, 7- and 8-methylflavones all adsorb iodine, but only the first three form mixed crystals (permanent blue needles), whilst in the other case the amorphous adsorption compound is gradually changed to colourless crystals. Simple substances, not obtainable in the amorphous condition, do not take up iodine unless they form mixed crystals with it (for example, coumarin).

The best known case of mixed crystals of iodine are those with benzene (Beckmann and Stock, *Zeitsch. physikal. Chem.*, 1895, **17**, 120).

Possibly alkaloidal periodides, like herapathite, are also mixed crystals, containing free iodine in non-stoicheiometrical proportion. Küster (*Zeitsch. physikal. Chem.*, 1895, **16**, 156) and Barger and Field have shown that cholalic acid does not form mixed crystals unless the concentration of the iodine in the solution exceeds a definite value. We have now observed a similar limit in other cases (for example, benzoylcoumarin), but the limit is sometimes so low as to be doubtful, as in the case of coumarin, which is not quite white when crystallised from dilute alcohol containing only $N/20{,}000$-iodine; at $N/500$ the crystals are bluish-grey. The range of miscibility varies greatly in different cases.

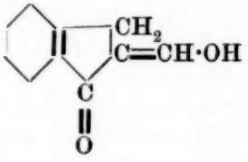
The most characteristic feature of the blue mixed crystals is their strong pleochroism, resembling that of herapathite. Owing to the kindness of Prof. W. J. Pope, F.R.S., for whose help our hearty thanks are due, this pleochroism could be observed in the case of coumarin, acetylcoumarin, benzoylcoumarin, coumarincarboxylic acid and narceine. It should be borne in mind that for the formation of mixed crystals isomorphism is not necessary (compare Bruni, "Feste Lösungen und Isomorphismus," Leipzig, 1908, p. 52).

Although mixed crystals are most readily obtained from mixtures of alcohol, or of acetic acid, with water, other solvents may be available. Thus narceine–iodine crystals are formed by adding

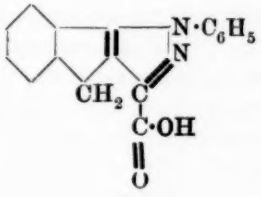
light petroleum to a pyridine solution, or chloroform to a glacial acetic acid solution of the components. As is further to be foreseen theoretically, mixed crystals also result from the vapour phase. Flavone and iodine, sublimed together at 1 mm., give metallic-looking needles, quite distinct from the iodine sublimate, and coumarin and iodine, kept side by side in a partial vacuum at room temperature, yield a deposit of curved filamentous mixed crystals.

Influence of Chemical Constitution on Adsorptive Power.

That there is a qualitative connexion between chemical constitution and power of adsorbing iodine is evident from the experimental part, for all the substances there mentioned are pyrone derivatives. Moreover, closely related substances (dihydrocoumarins, flavanones, xanthene) do not form blue additive compounds with iodine. Incidentally, we have found other substances, outside the pyrone group, which show an identical behaviour to iodine. These comprise quinones, phthaleins, and substances which, like the γ-pyrones, possess a crossed conjugated double linking, as in I and II:



(I.)



(II.)

Other examples are the crystalline di-, tri-, tetra-, and hexa-amyloses of Pringsheim and Eissler (*Ber.*, 1913, **46**, 2968), and the periodides of benzamide described by Moore and Thomas (*J. Amer. Chem. Soc.*, 1914, **36**, 1928).

A quantitative connexion between chemical constitution and adsorptive power is less obvious, although there is a well-marked favourable influence of aryl groups, as in the adsorption of aromatic substances by charcoal, etc. This favourable influence is shown by the limit of iodine adsorption; for substances with one benzene ring (phenylmethylpyrone, coumarin, benzo-γ-pyrone) it is roughly $N/100$—$N/1000$-iodine, for those with two benzene rings (diphenylpyrone, naphthapyrones, flavone) the limit is of the order of $N/10{,}000$; the naphthaflavones, with three benzene rings, are again about ten times as sensitive. It is noteworthy that the residual valency of iodine in aromatic compounds is greater than in aliphatic ones, as is shown by the existence of iodoso- and iodonium compounds.

The effect of alkyl groups, at least of the *iso*propyl group in methyl*iso*propyl-benzo-γ-pyrone and -flavone, is in the opposite direction, diminishing the power of forming blue iodine additive compounds. The introduction of hydroxyl groups in xanthone and of methoxy-groups in thioxanthone very greatly increases adsorption, but such regularities as can be deduced in the case of these and other substituents apply only within narrow limits, and remind one of the relationships observed between chemical constitution and physiological action. It may be indeed, that the often great differences in the action of closely related substances are caused by differences in their adsorption by the tissues. Furthermore, there are indications that substituents exert their effect on adsorptive power by determining the electrical state of the substance in colloidal solution.

From what has been said above it is probable that the addition of iodine by the organic substance is the result of residual affinity. We are unable to formulate the additive compound by means of ordinary valencies, such as are used for methyl iodide. We may, however, direct attention to the very interesting additive compounds of potassium and ketones and other substances lately described by Schlenk and his pupils (*Ber.*, 1913, **46**, 2840; 1914, **47**, 473, 1664). These compounds are highly coloured; chromone and xanthone, which add iodine, also add potassium. The power of taking up potassium is enhanced by aryl groups. Schlenk formulates some of his compounds with tervalent carbon, the potassium being attached to a previously ketonic oxygen atom.

Experimental.

In the following M.C. denotes mixed crystals, A.A. amorphous adsorption compound. Unless there is a statement to the contrary, alcoholic solutions of the substance were mixed with aqueous iodine solutions. The concentration of free iodine, at which adsorption takes place, is expressed by the number of litres containing 1 gram atom; thus 500 means $N/500$-iodine.

Derivatives of α-Pyrone.

Coumarin.—M.C.; blue pleochroic needles 500; pale grey 5000; not perfectly white 20,000.

Dicoumarin (3:3′-*Dicoumaryl*).—No M.C.; A.A. transitory 100.

3-*Acetylcoumarin* (*Acetocoumarin*).—M.C. plates, crystallographically similar to those of the substance itself, below 600; characteristic grey, metallic, with very strong pleochroism; orthorhombic (or possibly monosymmetric), iodine is orthorhombic. A.A.

pure blue, very transitory, from concentrated alcoholic solution at 1000, or by rapid cooling; changes to colourless crystals in a few seconds.

3. *Benzoylcoumarin.*—M.C. 300, strongly pleochroic blue needles, opaque when long axis parallel to plane of polarisation. At 100—200 in 20—30 per cent. alcohol on cooling, first large, colourless needles separate, and then, from separate centres, clusters of much smaller, very thin M.C.

Coumarin-3-carboxylic Acid.—M.C., similar to the above, from concentrated solution.

6-*Methylcoumarin-3-carboxylic Acid.*—M.C. below 500. A.A. black, from alkali at 50, violet from alcohol at 2000.

4 : 6-*Dimethylcoumarin.*—M.C. not formed. A.A. transitory, blue at 400.

Hydroxycoumarins.—7-*Hydroxy-(umbelliferone)*, 7-*hydroxy-4-methyl-*, 7-*hydroxy-3 : 4-dimethyl-*, 7 : 8-*dihydroxy-(daphnetin)*, and 7 : 8-*dihydroxy-4-methyl-coumarin* yield the reaction only when precipitated from concentrated solutions in alkali, not in alcohol; they are too soluble. The benzoyl derivatives of all these give blue compounds at 100, M.C. (filamentous curved needles) being observed in one case only, that of 7 : 8-dibenzoyloxy-4-methylcoumarin.

The behaviour of these substances may be illustrated by that of 7-hydroxy-4-methylcoumarin (easily obtained from resorcinol and ethyl acetoacetate by von Pechmann's method). The substance itself gives A.A. from alkaline solution with concentrated acid potassium tri-iodide, the methyl ether at 30 a reddish-brown precipitate. The latter dissolves on warming, and separates on slow cooling in colourless, on rapid cooling in grey mixed crystals. The acetyl derivatives could not be made to add iodine. A 0·1 per cent. solution of the benzoyl derivative in 90 per cent. alcohol mixed with ten volumes of iodine solution, becomes almost immediately dark blue at 1000, after a few seconds at 3000. At 5000 the white suspension acquires a blue tint after thirty seconds, and gradually becomes deep indigo-blue; at 10,000 the blue colour appears after fifty seconds. The A.A. is a very unstable negative lyophobic colloidal solution or suspension, instantly flocculated by traces of multivalent cations, for example, the calcium of tap-water; compare saponarin (Barger and Field, *loc. cit.*). On keeping for an hour or so the blue A.A. becomes white and microcrystalline; hence no M.C. The benzenesulphonyl derivative does not adsorb iodine, which fact corresponds with the observation by Freundlich ("Kapillarchemie," p. 160) that the introduction of a sulphonic acid group into a benzene ring lessens its adsorption by charcoal. Adsorbent and adsorbed substance are relative terms, like solvent and solute.

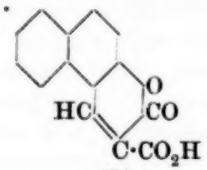
7-Benzoyloxy-4-methyl-3:4-dihydrocoumarin shows no affinity to iodine, as might be expected from the reduction of the pyrone ring.

7-Benzoyloxy-3:4-dimethylcoumarin is similar to the monomethyl derivative, but crystallises more rapidly. At 3000 adsorption in fifteen seconds, colourless crystals in twenty-five seconds after mixing.

Instead of by benzoylation, the affinity of hydroxycoumarins to iodine may be increased by introducing a phenyl group in the pyrone ring. *7-Hydroxy-4-phenylcoumarin* gives transitory blue A.A. at 1000.

In the *naphthapyrones* this affinity is further increased. With 4:3-β-naphthapyrone distinctly blue A.A. at 7000 at once; at 10,000 in neutral solution after a few minutes, in the presence of 0·01*N*-hydrochloric acid immediately. At 20,000 no coloration in neutral solution, but gradually in acid solution. Even 0·001*N*-acid has a favourable effect on adsorption.

4:3-β-Naphthapyrone-2-carboxylic acid (I) shows markedly the effect of cations on adsorption. At 2000 A.A. pale blue, with one drop of calcium chloride solution dark purple. At 10,000 in tap-water distinct coloration.



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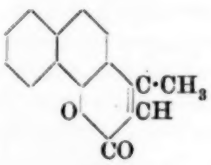
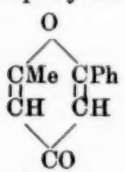


(II.)

4-Methyl-1:2-α-naphthapyrone (II) crystallises very rapidly. No M.C. Therefore at 5000 only a momentary blue. *2-Phenyl-4:3-β-naphthapyrone* at 1000 dark blue after thirty minutes, but only in the presence of multivalent cations (*M*/1000-$AlCl_3$) or hydrogen ions (0·1*N*-HCl).

Derivatives of γ-Pyrone.

2-Phenyl-6-methylpyrone (III).—M.C. at 10 after half-an-hour, more rapidly in the presence of acid.



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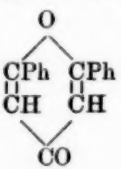

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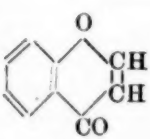


(V.)

2:6-*Diphenylpyrone* (IV).—A.A. up to 20,000; no M.C.

Benzo-γ-pyrone (V).—Crimson to purple coloration at 1000.

Benzo-γ-pyrone-2-carboxylic Acid.—Crimson coloration at 1000. M.C. (pleochroic needles) from warm dilute alcohol. A solution of the sodium salt, if at least decinormal, gives on acidification in the presence of iodine the typical blue A.A. From alcohol the acid crystallises too rapidly.

6-*Methylbenzo-γ-pyrone-2-carboxylic Acid.*—Sodium salt at least 0·005 normal and acid iodine up to 50 gives blue A.A., rapidly becoming colourless and crystalline. The same momentarily on rapidly cooling an alcoholic solution. Therefore no M.C., in contradistinction to the preceding.

7-*Methylbenzo-γ-pyrone-2-carboxylic Acid.*—Like the above, but adsorption and crystallisation take place still more slowly. With concentrated solution in glacial acetic acid black A.A. at 10. From alkali at 10,000 white precipitate, which slowly becomes pure blue and then gradually changes to colourless crystals. No M.C.

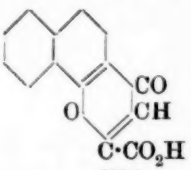
8-*Methylbenzo-γ-pyrone-2-carboxylic acid* shows the same limit 10,000 when precipitated from alkaline solution.

6 : 8-*Dimethylbenzo-γ-pyrone-2-carboxylic acid* gives a crimson-purple A.A. from alkaline solution at 1000—10,000, and a blue one below 500 (unless much potassium iodide is present, when the A.A. is always crimson; compare Barger and Field, *loc. cit.*, p. 1403).

5-*Methyl*-8-iso*propylbenzo-γ-pyrone-2-carboxylic acid* shows still more markedly the effect of alkyl groups; no blue A.A. at all; at 10 only brown, amorphous precipitate.

1 : 4-α-*Naphthapyrone* (from the acid VI, below) crystallises extremely rapidly. At 20,000 a blue flash (A.A.) can just be detected, before colourless crystals appear. At 1000, on rapid cooling, blue flakes and colourless crystals appear together. The former slowly disappear, more slowly in the presence of gelatin, which acts as a protective colloid.

1 : 4-α-*Naphthapyrone-2-carboxylic Acid* (VI).—Limits 5000 from glacial acetic acid, 20,000 from alkali. Adsorption slow.



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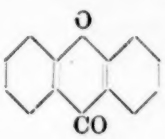


(VII.)

Xanthone Derivatives.

In no cases M.C. *Xanthone* (VII) has limits 500 in neutral, 1000 in *N*/10-acid solution.

3-*Hydroxyxanthone* is even less sensitive than the parent substance. Faint purple coloration at 200, from alkali only.

2-*Hydroxyxanthone*, on the other hand, has limits 6000 (alcohol) and 10,000 (alkali). 2:4- and 4:6-*Dihydroxyxanthones* behave similarly. The latter substance, which gives a greenish-blue coloration, is euxanthone, of which *euxanthic acid* is the glycuronic acid derivative. It was in preparing the esters of this acid, by means of alkyl iodides, that Graebe (*Ber.*, 1900, **33**, 3360) observed the formation of blue iodine compounds. The property of giving these is, however, not confined to the esters, as Graebe imagined. Iodine is also adsorbed by the acid, provided the latter is in colloidal solution. It can be obtained in this condition by acidifying dilute solutions of its salts or by rapidly cooling its hot saturated solution in water. The sols, so obtained, are unstable, and soon crystallise. They are coloured blue by iodine, and are then more or less suddenly decolorised by dilution to about 1:5500, when the whole of the acid is in the molecular-disperse condition, for by shaking with water we found the true solubility to be about 1:7000. The approximate agreement between these values once more shows that molecular-disperse solutions are not coloured blue, because they do not adsorb; a similar agreement was found by Barger and Field for the glucoside saponarin. That adsorption is dependent on the amorphous state results from the following. The long, yellow needles of the acid, obtained from dilute alcohol, break up, when placed in water, into an amorphous suspension, which is coloured blue by iodine. In a few minutes this changes to small, lancet-shaped crystals, which are no longer so coloured. The adsorption of iodine by sols of euxanthic acid is markedly favoured by multivalent cations.

β-Phenonaphthaxanthone (m. p. 149°, from betol, Graebe and Feer, *Ber.*, 1886, **19**, 2612).—A.A. at 200 from neutral, at 5000 from acid solution.

α-Dinaphthaxanthone (dinaphthylene-ββ-ketone-αα-oxide, m. p. 240°, from α-naphthol-β-carboxylic acid).—A.A. at 20,000, on keeping slightly at 50,000.

Flavone Derivatives.

Flavone.—Immediate black A.A. at 10—100; at 4000 at first colourless precipitate, partly changed in a few minutes to blue needles. M.C. also obtained by sublimation. Formation of blue A.A. and M.C. favoured by acids; with *N*-hydrochloric acid at once at 8000, on keeping at 20,000.

6- and 7-*Methylflavones* behave quite similarly; blue, filamentous M.C. slowly at 2000. 8-*Methylflavone*, on the other hand, does not

form M.C. The blue A.A. given almost immediately at 1000, changes in a few minutes to colourless crystals. All three methylflavones are five to ten times as sensitive in *N*-hydrochloric acid as in neutral solution.

5-*Methyl*-8-iso*propylflavone* has a much smaller affinity for iodine (compare 5-methyl-8-*iso*propylbenzo-γ-pyrone-2-carboxylic acid, above). Adsorption takes place very slowly, but becomes evident rather suddenly, as if after an induction period. Thus at 30 the amorphous precipitate, after showing no obvious change for about thirty seconds, becomes deep bluish-green with striking rapidity. At 100—200 this occurs after five minutes, at 500 after ten minutes. Multivalent cations and acids delay or prevent this colour change, whereas multivalent anions (citrate, phosphate, ferricyanide, sulphate) accelerate adsorption, so that at 100 it is evident in a few seconds. The influence of cations and anions and of acids on adsorption is here the reverse of that usually found; we hope to connect it with the electrical properties of the colloidal substance.

8-*Hydroxyflavone*, coloration at 10 in neutral solution, transitory bluish-green A.A. at 500 in acid solution. No M.C.

3′-*Hydroxyflavone* from alkali slowly at 8000; 4′-*hydroxyflavone* from alkali at once at 25,000.

6:4′-*Dihydroxyflavone* transitory A.A. at 1000. No M.C.

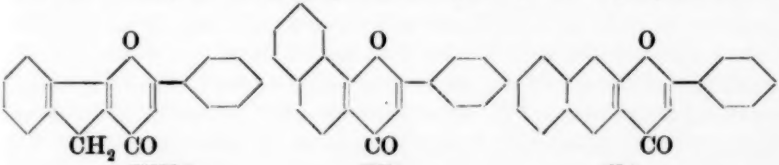
5:7-*dihydroxyflavone* (*chrysin*).—Neutral slowly at 10,000 pale blue, in 0·1*N*-hydrochloric acid at once deep blue.

5:7:4′-*Trihydroxyflavone* (*apigenin*) from alkali at once purplish-black at 2000, on keeping at 5000. *Saponarin* or vitexin glucoside, closely related to the preceding, at 4000 from alkali.

7:3′:4′-*Trihydroxyflavonol* (*fisetin*).—From concentrated solution in alkali black at 10, slowly dark green at 100. This is the only substance examined containing a hydroxyl group in the pyrone ring.

2′:3′-*Dimethoxyflavone* gives no typical reaction with iodine. 7:3′-*Diethoxyflavone* at 100 purplish-brown, at 5000 crimson-purple, changing to blue in a few minutes, at 10,000 first yellow, afterwards pale blue.

With *indenoflavone* (VIII) and *α-naphthaflavone* (IX) the reac-



(VIII.) (IX.) (X.)

tion is more delicate than with starch itself, which gives no colour beyond 50,000 or 60,000. A few drops of a 0·1 per cent. alcoholic

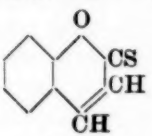
solution of indenoflavone added to 5 c.c. of iodine solution gives a blue colour below 10,000. At 10,000 this colour gradually changes to pink, at 40,000—60,000 it is at once pink. In the presence of multivalent cations the limit is 125,000. (Starch solutions are not rendered more sensitive by adding electrolytes.) α-Naphthaflavone gives pure blue colorations up to 80,000 in neutral, up to 100,000 in acid solution or in the presence of multivalent cations, on keeping at 150,000. At such extreme dilution there is less than one part of iodine per million of solution, and the flavone is less than 1:100,000. The A.A. remains in colloidal solution.

β-Naphthaflavone (X) is much less sensitive. In neutral solution no typical coloration at 10, in acid solution blue at 10,000. The difference from indenoflavone and α-naphthaflavone is probably connected with the impossibility of representing it with the usual alternation of double and single bonds in both the naphthalene and the pyrone nucleus (compare also Willstätter, *Ber.*, 1911, **44**, 3431). We have observed analogous differences in other isomerides, to be described later.

Flavanones, with a reduced pyrone ring, are indifferent to iodine, for example, 6-ethoxy- and 7:3′:4′-trimethoxy-flavanone, also 2′-methoxy- and 3′-methoxy-2′-hydroxy-α-naphthaflavanone.

Pyrone Derivatives containing Sulphur.

Thiocoumarin (XI) at 100—1000, dark-coloured precipitate, changing to grey crystals, like those of coumarin:



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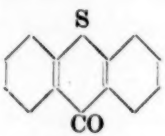


(XII.)

Thioxanthone (XII) crystallises very rapidly, and is not coloured even at 10.

Methylthioxanthone (Davis and Smiles, T., 1910, **97**, 1297), black A.A. at 10, reddish-brown, colloidal solution at 100.

1:4-*Dimethylthioxanthone.*—Slow adsorption at 100. In the presence of calcium chloride at once blue at 100, slowly at 1000.

2:4-*Dimethylthioxanthone.*—M.C. at 10—100.

Methoxythioxanthone (Davis and Smiles, *ibid.*, 1290) is much more sensitive. At 100 at once deep blue, at 3000 after some minutes; with calcium or hydrogen ions at 10,000.

1:4-*Dimethoxythioxanthone* is still more sensitive. At 30,000 a green colour in a few seconds, with calcium chloride at once blue.

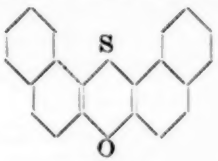
2-*Hydroxythioxanthone* up to 500. 2-*Methyl*-(5, 6, 7 or 8)-*mono*-

hydrothioxanthone up to 10,000. The 1-*hydroxy*-4-*ethoxy*-compound did not unite with iodine; the *chloromethoxy*-derivative [1:4 (?); Marsden and Smiles, T., 1911, **99**, 1356] adsorbed up to 10,000, as did *naphthathioxanthone* (*ibid.*, 1298).

β-Aminonaphthathioxanthone (*ibid.*, 1299) gives up to 1000 in neutral solution a dirty-green coloration, but in the presence of acetic acid, or 0·01—0·002*N*-hydrochloric acid a reddish-brown coloration appears slowly even at 100,000.

The *thioxin oxides*, in which sulphur replaces the carbon of the carbonyl group, have the same arrangement of linkings as the xanthones, and likewise adsorb iodine; for example, 3:6-*dimethylphenothioxin oxide* gives deep blue M.C. at 20.

The thioxins themselves, on the other hand, have no crossed conjugated double bond. *Naphthathioxin* (XIII) gives only a reddish-brown coloration, but on boiling this becomes bluish-green,



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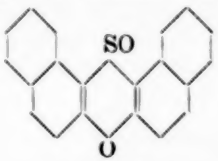

(XIV.)

owing to partial oxidation to the *oxide* (XIV), which is coloured deep blue at 100 and gives grey M.C. at 1000. iso*Naphthathioxin oxide* (Nolan and Smiles, T., 1913, **103**, 910) does not do this, presumably because it has a different carbon skeleton; the nature of the isomerism is unknown. Also, *naphthathioxin dioxide* (the sulphone) does not adsorb iodine.

Thioflavones.

Thioflavone forms M.C. At 1000 very slowly deep blue in neutral, at once in acid solution. 6-*Methylthioflavone* slowly at 5000—10,000. 5:8-*Dimethylthioflavone* gives A.A. at 300 after some minutes, but is one hundred times more sensitive in acid solution (at once at 10,000, after some minutes at 30,000). Adsorption is not effected by calcium chloride, but a minute increase in the concentration of the hydrogen ions makes a difference. Thus in the presence of 0·0001*N*-hydrochloric acid a definite blue coloration results after half-an-hour, whilst without the acid the substance remains colourless. This concentration of acid is much below that affecting Congo-red.

6:8-*Dimethylthioflavone* similarly adsorbs at 200 in neutral, at 20,000 in acid solution.

8-*Hydroxythioflavone*, only in acid solution up to 30.

6-*Methoxythioflavone*, 30,000 in neutral, 50,000 in acid solution.

8-*Methoxythioflavone* is much less sensitive than the above isomeride; limits 1000 and 5000 respectively.

α-Thionaphthaflavone (compare formula XI) up to 100,000 in acid solution. Resembles the oxygen compound, but adsorption takes place very slowly. *β-Thionaphthaflavone* (compare formula XII) is coloured blue at 1000 in neutral, at 100,000 in acid solution.

In general, the thioflavones are similar to the oxygen compounds, but adsorption takes place more slowly, and is much more influenced by the hydrogen-ion concentration of the solution.

We desire to tender our hearty thanks to Prof. W. J. Pope, F.R.S., for his valuable crystallographic help, and to Dr. S. Ruhemann, F.R.S., to Dr. S. Smiles, and to Prof. J. Tambor, of Berne, for their liberality in supplying us with specimens. Part of the expenses of the investigation were met out of a grant from the Research Fund of the Chemical Society, hereby gratefully acknowledged.

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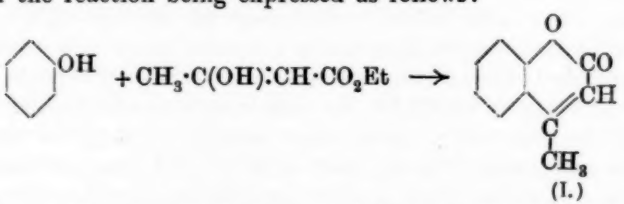
[*Received December 12th*, 1914.]

XLIX.—*Syntheses of Benzo-γ-pyrones and Flavones. Part I.*

By SERGE JACOBSON and BROJENDRANATH GHOSH.

IT has been shown by von Pechmann and his collaborators that substituted coumarins are formed when ethyl acetoacetate is condensed with phenols in the presence of sulphuric acid, the mechanism of the reaction being expressed as follows:

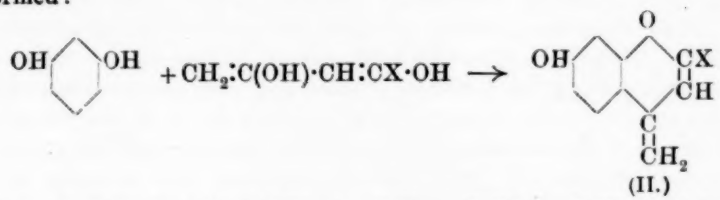


(I.)

This reaction appears to be accepted as a general one (compare Fries and Klostermann, *Annalen*, 1908, **362**, 3). Thus Simonis and his collaborators (*Ber.*, 1913, **46**, 2014; 1914, **47**, 2229)

assume that with sulphuric acid as condensing agent substituted acetoacetates give only coumarins.

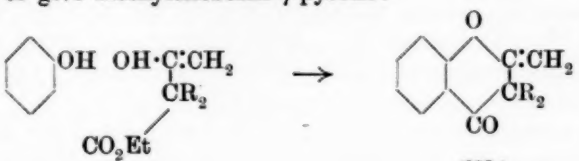
Bülow and Wagner (*Ber.*, 1900, **34**, 1198) have shown that by passing hydrogen chloride into a mixture of a *m*-dihydroxyphenol and acetyl- or benzoyl-acetone methylene-substituted pyrones are formed:



(II.)

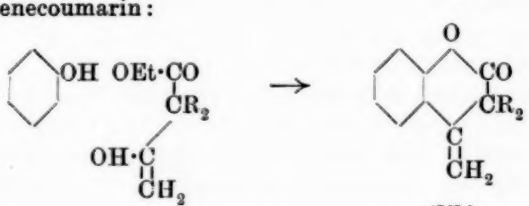
where x may be either CH_3 or C_6H_5. Collie and White * have obtained similar compounds from orcinol and acetylacetone.

In analogy to this reaction it was thought that by substituting both the active hydrogen atoms in ethyl acetoacetate by alkyl groups the course of the condensation with phenols might be changed to give methylenebenzo-γ-pyrone:



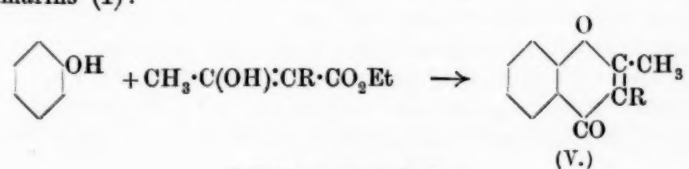
(III.)

or methylenecoumarin:



(IV.)

However, the expectation was not fulfilled, the condensation of resorcinol and dimethylacetoacetic ester in sulphuric acid not taking place at all. This does not exclude the possibility that with mono-substituted ethyl acetoacetates the condensation might proceed otherwise, giving benzo-γ-pyrones (V), instead of coumarins (I):



(V.)

* Private communication.

The possible occurrence of these reactions depends to a large extent on the reactivity of the methylene hydrogen atoms in ethyl acetoacetate. It is well known that by substituting one of the hydrogen atoms by different alkyl groups the reactivity of the remaining hydrogen is considerably diminished. The hope was entertained that by sufficiently diminishing the reactivity of the hydrogen atom the reaction might be induced to proceed as shown above. With this object in view one of the authors some time ago attempted to condense ethyl ethylacetoacetate with resorcinol, and found that the product was a mixture; the analysis was satisfactory, but the substance did not melt sharply even after many recrystallisations. It was therefore regarded as a mixture of a benzo-γ-pyrone and a coumarin.

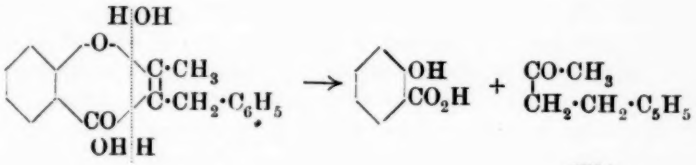
In the case of unsubstituted and methyl-substituted acetoacetic esters the products are coumarins, whereas with ethyl ethylacetoacetate a mixture is obtained. In view of the fact that as the complexity of the α-substituent is increased the reactivity of the remaining hydrogen atom is diminished, it was thought that with substituents of greater molecular weight the product would be solely a benzo-γ-pyrone. In the preliminary experiments we selected the benzyl group as the complex substituent, and, as anticipated, benzo-γ-pyrones were obtained.

These facts show that the course of the condensation is changed by the nature of the α-substituent. It is possible that when there is no substitution the reactivity of the hydrogen is very great and the hydroxyl group of the ester condenses at once with the hydrogen atom in the ortho-position with respect to the hydroxyl group of the phenol; subsequently, a molecule of alcohol is eliminated, as in I. Now, when the reactivity of the remaining methylene hydrogen atom in a mono-substituted ethyl acetoacetate has been diminished by the substitution, it cannot condense with hydrogen of the benzene nucleus, but is eliminated with the hydrogen of the phenolic hydroxyl group, and afterwards, to close the ring, ethyl alcohol is split off as in V.

In this paper, the products obtained by condensing ethyl benzylacetoacetate with resorcinol, *m*-cresol, pyrogallol, orcinol, phloroglucinol, and α-naphthol are described, the condensing agent being sulphuric acid in all cases. We have found, in agreement with Bülow's and Collie's results, that the condensation proceeds well with *m*-dihydroxyphenols, whereas with other phenols the yield is poor; *p*-cresol does not yield any condensation-product. The products contain a small amount of methylindenecarboxylic acid, which is formed by the internal condensation of ethyl benzyl-

acetoacetate (Pechmann, *Ber.*, 1883, **16**, 516; Roser, *Annalen*, 1888, **247**, 157).

In order to prove the constitution of the compounds they were decomposed with alkali. The reaction may be explained as follows:



(VI.)

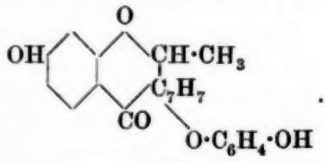
giving a hydroxy-acid and a neutral ketone—benzylacetone. The decomposition of a coumarin would produce a hydroxy-ketone and phenylpropionic acid or a hydroxycoumaric acid, and in both cases the products would be soluble in alkali. A neutral ketone is obtained, giving the characteristic sodium hydrogen sulphite additive product and the semicarbazone of benzylacetone; the hydroxy-acids of the corresponding phenols have also been isolated and identified by the preparation of characteristic derivatives.

Benzo-γ-pyrones and flavones have hitherto been synthesised by the indirect and difficult processes of Kostanecki, Tambor, Nagai, Ruhemann, Simonis, and others. The present method may serve as a simple and useful way of preparing the substituted benzo-γ-pyrones and flavones occurring in many natural colouring matters.

On consulting the literature of the subject it was found that, with one exception, no one has attempted to condense phenols with substituted acetoacetates other than the methyl acetoacetate. Fries and Klostermann (*loc. cit.*, p. 27) incidentally described the condensation of ethyl ethylacetoacetate and ethyl benzylacetoacetate with *m*-cresol, and assumed that the products were 3:4:7-tri-substituted coumarins. Repeating their experiments, we have not been able to isolate, in the case of ethyl ethylacetoacetate and *m*-cresol, the product described by them as melting at 87°, but always obtained a substance melting at 130°, even when the quantity of sulphuric acid was doubled. The determination of the molecular weight seems to show that this is an additive product containing one molecule of *m*-cresol attached to the condensation product, but its properties have not been further investigated. In the case of *m*-cresol and ethyl benzylacetoacetate we obtained the compound described by these authors, but since it is decomposed by alkali, yielding benzylacetone, the substance has a benzo-γ-pyrone structure, and is not 3-benzyl-4:7-dimethylcoumarin, but 3-benzyl-2:7-dimethylbenzo-γ-pyrone.

In some instances Simonis and his colleagues (*loc. cit.*) have obtained benzo-γ-pyrones and flavones in poor yield by using a drastic condensing agent, such as phosphoric oxide and by effecting the condensation at 110—160°. They emphasise the importance of the condensing agent, although they were not able to obtain any results with unsubstituted esters. In the earlier part of this paper we gave our explanation of the influence of the substituent on the direction of the condensation. Simonis's work supports this view to some extent. In ordinary instances, using sulphuric or hydrochloric acid or zinc chloride, methylacetoacetic ester gives a practically pure coumarin, whereas with a very strong condensing agent and with substituted esters such as methyl- or sodium-aceto- and benzoyl-acetates it is possible to change the course of the reaction and to produce a benzo-γ-pyrone. However, it is impossible to do so with unsubstituted aceto- and benzoyl-acetic esters. It is apparent that the most effective factor influencing the direction of the condensation is substitution, the condensing agent playing a secondary, although important, part.

We have found that by varying the conditions of the reaction a compound can be isolated containing one molecule of phenol attached to the benzo-γ-pyrone nucleus. Fries and Klostermann (*loc. cit.*, p. 13) have isolated, in the case of 4:7-dimethylcoumarin, an additive product which they have named tolyloxy-4:7-dimethylcoumarin. According to their view, the additive product, for example, of resorcinol and 7-hydroxy-3-benzyl-2-methylbenzo-γ-pyrone, is represented by the formula:



(VII.)

Experimental.

7-Hydroxy-3-benzyl-2-methylbenzo-γ-pyrone.

A mixture of 3 grams of resorcinol and 5 grams of ethyl benzylacetoacetate was treated with about 20 c.c. of sulphuric acid (D 1·85) in small portions, the mixture being cooled during the addition. The resorcinol dissolved slowly to a yellowish-brown solution, which was allowed to remain overnight. The solution was then poured on ice, and the precipitate collected, washed, and crystallised from alcohol. The product melted indefinitely at 175—185° owing to the presence of methylindenecarboxylic acid.

The crude product was therefore dissolved in dilute sodium hydroxide and precipitated by carbon dioxide, the precipitate collected, washed with water, and crystallised from dilute alcohol, being then obtained in long, yellowish needles, melting at 186°. The yield of the crude product in this and other cases is about 75—85 per cent., and of the pure product about 55—65 per cent. of the theoretical. The compound develops an intensively bluish-violet fluorescence in concentrated sulphuric acid, and a faintly blue fluorescence in alkali:

0·1375 gave 0·3735 CO_2 and 0·0674 H_2O. C=74·08; H=5·44.
$C_{17}H_{14}O_3,\frac{1}{2}H_2O$ requires C=74·18; H=5·45 per cent.

The water of crystallisation could not be estimated in the direct way, the compound subliming at 120°.

The solution remaining after precipitating the compound with carbon dioxide was acidified with dilute sulphuric acid and the precipitate crystallised from acetic acid. It melted at 200°, and was undoubtedly methylindenecarboxylic acid (Found, C=75·75; H=5·70. $C_{11}H_{10}O_2$ requires C=75·80; H=5·74 per cent.)

An *acetyl* derivative was prepared from the benzo-γ-pyrone by boiling with acetic anhydride and fused sodium acetate. The compound crystallised from alcohol in long, silky needles containing $\frac{1}{2}H_2O$ and melting at 168°, but was obtained anhydrous from acetic acid:

0·1440 gave 0·3792 CO_2 and 0·0680 H_2O. C=71·82; H=5·09.
$C_{19}H_{16}O_4,\frac{1}{2}H_2O$ requires C=71·92; H=5·36 per cent.

The *benzoyl* derivative was prepared by the Schotten-Baumann method in pyridine solution. It crystallised from alcohol in soft, long needles, melting at 150°:

0·1288 gave 0·3504 CO_2 and 0·0576 H_2O. C=74·19; H=4·97.
$C_{24}H_{18}O_3,H_2O$ requires C=74·23; H=5·16 per cent.

The methyl and ethyl ethers were prepared by shaking the solution of the substance in sodium hydroxide with rather more than the calculated quantity of methyl or ethyl sulphates. The *methyl ether* crystallises from acetic acid in short, white needles, which melt at 119°:

0·1304 gave 0·3684 CO_2 and 0·0680 H_2O. C=77·04; H=5·79.
$C_{18}H_{16}O_3$ requires C=77·10; H=5·71 per cent.

The *ethyl ether* crystallises from alcohol in long, thin needles, melting at 145°:

0·1211 gave 0·3438 CO_2 and 0·0683 H_2O. C=77·43; H=6·27.
$C_{19}H_{18}O_3$ requires C=77·55; H=6·12 per cent.

Both the ethers show the same fluorescence in concentrated sulphuric acid as the parent compound.

In order to prove the constitution the substance was decomposed with alkali. Three grams were boiled with a solution of 15 grams of potassium hydroxide in 30 c.c. of water under a reflux condenser for four hours, and after being cooled the liquid was extracted with ether. The ethereal solution on evaporation left an oil which gave a crystalline compound on shaking with concentrated sodium hydrogen sulphite solution. This was collected and decomposed by dilute alkali, and the oil obtained was shaken with an excess of a solution of semicarbazide hydrochloride and sodium acetate. The crystalline product was collected, washed, and recrystallised from a mixture of benzene and petroleum, and was thus obtained in fine, soft needles, melting at 140—141° (Found, N = 20·7. $C_{11}H_{15}ON_3$ requires N = 20·5 per cent.). The semicarbazone of benzylacetone melts at 142° (*Ber.*, 1904, **37**, 2313).

The alkaline solution was acidified with dilute sulphuric acid, and the precipitate was found to be a mixture of the decomposition product and the unchanged substance. In order to separate them, the whole was dissolved in sodium hydroxide, and the unchanged substance was precipitated by passing carbon dioxide. This was filtered off, and the solution acidified again and extracted with ether. On evaporation the ethereal solution left a solid residue, which crystallised from hot water in white prisms melting at 202—203°; the melting point of anhydrous β-resorcylic acid is 204—206° (*Ber.*, 1885, **18**, 1985). The silver salt of the acid was prepared and analysed (Found, Ag = 41·38. Calc., Ag = 41·38 per cent.).

Thio-derivative.

A thio-derivative was prepared from 7-hydroxy-3-benzyl-2-methylbenzo-γ-pyrone by fusing 2 grams of the substance with the same weight of phosphorus pentasulphide in an oil-bath at the temperature of its melting point. The fusion was powdered and extracted with boiling chloroform, the dark solution being boiled for six hours with animal charcoal and copper powder, filtered, and the chloroform distilled off. The viscous, oily residue was dissolved in glacial acetic acid, and by dilution with water a substance was obtained in brick-red prisms melting and decomposing at 198°. The analysis indicates that the oxygen of the carbonyl and of the hydroxyl group of the benzo-γ-pyrone has been displaced by sulphur:

0·1205 gave 0·1884 $BaSO_4$. S = 21·46.

$C_{17}H_{14}OS_2$ requires S = 21·81 per cent.

7-Hydroxy-3-m-hydroxyphenoxy-3-benzyl-2-methylbenzo-γ-pyrone (VII).

By diminishing the quantity of sulphuric acid in the condensation another product is formed, containing a molecular proportion of resorcinol attached to the benzo-γ-pyrone nucleus. Three grams of resorcinol and 5 grams of ethyl benzylacetoacetate were slowly treated at 0° with 5 c.c. of sulphuric acid, and after keeping overnight, the brown mixture was poured on ice. The precipitate was collected and was crystallised from dilute acetic acid, from which it separated in short, yellow, glistening prisms, melting at 224°:

0·1294 gave 0·3650 CO_2 and 0·0644 H_2O. C = 73·84; H = 5·53.
0·1155, in 17·80 naphthalene, gave $\Delta^t = -0·132°$. M.W. = 342.
0·1756, „ 8·8 c.c. ethyl alcohol, „ $\Delta^t = \cdot\ 0·08°$. M.W. = 389.
$C_{23}H_{20}O_5$ requires C = 73·40; H = 5·32 per cent. M.W. = 376.

On dissolving the compound in sulphuric acid and keeping for some time or heating a very intense bluish-violet fluorescence is developed. Boiling with dilute sulphuric or concentrated hydrochloric acid does not decompose the substance, but concentrated sulphuric acid sulphonates it, the product being an oil.

The acetyl derivative obtained by boiling the compound (VII) with acetic anhydride and sodium acetate is identical with the acetyl derivative of 7-hydroxy-3-benzyl-2-methylbenzo-γ-pyrone:

0·1225 gave 0·3329 CO_2 and 0·0594 H_2O. C = 74·11; H = 5·38.
$C_{19}H_{16}O_4$ requires C = 74·03; H = 5·20 per cent.

3-Benzyl-2:7-dimethylbenzo-γ-pyrone.

This compound was prepared from *m*-cresol and ethyl benzylacetoacetate. Three grams of *m*-cresol were condensed with 5 grams of the ester in the same way as described in the case of resorcinol. The crude product was freed from methylindenecarboxylic acid, and was crystallised from alcohol. The substance separates in long, white needles, melting at 117°, and develops a green fluorescence in concentrated sulphuric acid (Found, C = 81·79; H = 5·91. $C_{19}H_{16}O_2$ requires C = 81·81; H = 6·06 per cent.).

This is evidently the compound described by Fries and Klostermann (*loc. cit.*, p. 27) as a coumarin. Its constitution was proved as follows: Three grams of the substance were decomposed in the manner described above, except that the alkali was more concentrated (20 grams in 20 c.c. of water), and benzylacetone was isolated and identified by its semicarbazone (m. p. 141°).

In an attempt to prepare the substance obtained by Fries from *m*-cresol and ethyl ethylacetoacetate, we repeated the condensation under his conditions, but the product melted at 130°, not at 87°, as

stated by him. Molecular-weight determination shows this to be an additive compound, containing one molecule more of *m*-cresol:

0·1478, in 11 c.c. ethyl alcohol, gave $\Delta^t = 0·065°$. M.W. = 322.
0·2224, „ 15·9 c.c. benzene, gave $\Delta^t = 0·15°$. M.W. = 301.
$C_{20}H_{22}O_3$ requires M.W. = 310.

3-Benzyl-2-methyl-1 : 4-α-naphthapyrone.

Four grams of α-naphthol were condensed with 6 grams of ethyl benzylacetoacetate, and the product was purified in the way described above. When the sulphuric acid solution was poured on ice, the compound separated as an oil, which solidified on stirring. The substance develops a sea-green fluorescence in concentrated sulphuric acid, and is insoluble in cold alkali. It crystallises from a large volume of alcohol in yellow needles, melting at 187°:

0·1311 gave 0·4034 CO_2 and 0·0637 H_2O. C = 83·92; H = 5·39.
$C_{21}H_{16}O_2$ requires C = 84·00; H = 5·33 per cent.

The decomposition with alkali was effected in the manner described above. After boiling 3·5 grams of the substance with 20 grams of potassium hydroxide in 20 c.c. of water for eight hours, the solution was distilled in a current of steam, and the distillate extracted with ether. The oil obtained after evaporation of the ether gave a *semicarbazone*, which was crystallised from a mixture of benzene and light petroleum, and melted at 141°:

0·0663 gave 12·0 c.c. N_2 at 20° and 758 mm. N = 20·65.
$C_{11}H_{15}ON_3$ requires N = 20·49 per cent.

From the alkaline solution an acid was obtained which was crystallised from dilute alcohol, and then melted at 187°, which is the melting point of 1-naphthol-2-carboxylic acid (*Ber.*, 1887, **20**, 2699),* and a mixture of the two acids melted at the same temperature. A characteristic ammonium salt was prepared; it crystallised in long, colourless needles from hot water, and melted with decomposition at 221°:

0·1458 gave 8·8 c.c. N_2 at 18° and 756 mm. N = 6·94.
$C_{11}H_{11}O_3N$ requires N = 6·83 per cent.

7 : 8-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone.

This was prepared by condensing 3 grams of pyrogallol and 5 grams of benzylacetoacetic ester in the usual way. The solution,

* An acetyl derivative prepared from this acid and also from α-naphthol-carboxylic acid by boiling with sodium acetate and acetic anhydride melted at 143°. The only reference to this derivative (Schmitt and Burkard, *loc. cit.*, p. 2700) records the melting point 158°, but the method of preparation is not stated and no analysis of the compound is given.

which becomes dark red, must be thoroughly cooled. The compound was crystallised from alcohol, and melts at 185°. It develops a green fluorescence in concentrated sulphuric acid and in dilute alkali:

0·1211 gave 0·3022 CO_2 and 0·0583 H_2O. C = 68·06; H = 5·35.
$C_{17}H_{14}O_4,H_2O$ requires C = 68·00; H = 5·33 per cent.

The *acetyl* derivative, prepared in the usual way, crystallises from dilute acetic acid in white, hard prisms melting at 172°:

0·1203 gave 0·3034 CO_2 and 0·0546 H_2O. C = 68·78; H = 5·04.
$C_{21}H_{18}O_6$ requires C = 68·85; H = 4·92 per cent.

The *benzoyl* derivative crystallises from acetic acid in needles melting at 184°:

0·1310 gave 0·3630 CO_2 and 0·0545 H_2O. C = 75·57; H = 4·62.
$C_{31}H_{22}O_6$ requires C = 75·91; H = 4·48 per cent.

*7-Hydroxy-3-benzyl-2:5-dimethylbenzo-γ-pyrone.**

This was prepared from orcinol and ethyl benzylacetoacetate, and purified in the usual way. When crystallised from acetic acid it separated in short, white needles, melting at 177—178°:

0·1275 gave 0·3610 CO_2 and 0·0672 H_2O. C = 77·22; H = 5·85.
$C_{18}H_{16}O_3$ requires C = 77·14; H = 5·71 per cent.

The *acetyl* derivative crystallises from dilute acetic acid in hard, short needles, melting at 169°:

0·1009 gave 0·2746 CO_2 and 0·0509 H_2O. C = 74·22; H = 5·60.
$C_{20}H_{18}O_4$ requires C = 74·53; H = 5·59 per cent.

The *benzoyl* derivative solidifies after keeping for some days in dilute sulphuric acid, and when crystallised from glacial acetic acid melts at 119—120°.

5:7-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone.

This was prepared from phloroglucinol and ethyl benzylacetoacetate. It crystallises from acetic acid in hard, short needles, melting at 218—219°, and develops a green fluorescence in sulphuric acid. The sample for analysis was dried in a steam-bath:

0·1173 gave 0·2984 CO_2 and 0·0508 H_2O. C = 69·39; H = 4·81.
$C_{17}H_{14}O_4,\frac{1}{2}H_2O$ requires C = 69·30; H = 4·70 per cent.

The *acetyl* derivative crystallised from acetic acid in long, silky needles, melting at 154°:

* Many of the benzo-γ-pyrones in this series have almost identical melting points. To avoid error, melting points of mixtures of the substances were determined and depressions of 30° and more were observed.

0·1317 gave 0·3312 CO_2 and 0·0585 H_2O. C = 68·58; H = 4·93.
$C_{21}H_{18}O_6$ requires C = 68·85; H = 4·92 per cent.

This research is being extended in many directions, and condensations of a similar nature to those described above are in progress.

We take this opportunity to express our sincere gratitude to Dr. S. Smiles and Dr. W. B. Tuck for their interest and encouragement during the investigation.

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LONDON.

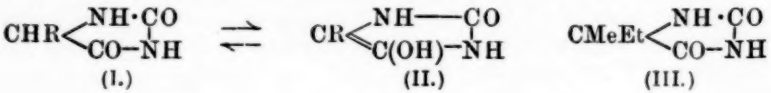
[*Received March 4th*, 1915.]

L.—*The Constitution of Allantoin and Allied Substances.*

By HENRY DRYSDALE DAKIN.

THE customary formula for allantoin (IV), based largely on Grimaux's synthesis from glyoxylic acid and carbamide, contains an asymmetric carbon atom, and hence allantoin would be expected to be capable of existence in optically active forms. Mendel and the author (*J. Biol. Chem.*, 1910, **7**, 153) have shown that naturally occurring allantoin, isolated from urine with a minimum of chemical manipulation, is optically inactive. Furthermore, attempts to resolve allantoin into an active component by bacterial action gave negative results.

The natural occurrence of optically inactive substances containing asymmetric carbon atoms is rare, so that it was of interest to endeavour to determine the cause of the inactivity of allantoin. Now allantoin, according to Grimaux's formula, is represented as a substituted hydantoin, and the author (*Amer. Chem. J.*, 1910, **44**, 48) has shown that optically active hydantoins of the most varied kind, containing a hydrogen atom linked to carbon (I), undergo racemisation with extraordinary ease, at room temperature, especially but not exclusively in the presence of alkali. The cause of the racemisation was shown, apparently conclusively, to be due to tautomeric change of the keto-enol type, the enol form (II) being produced in low concentration with loss of asymmetry:



(I.) (II.) (III.)

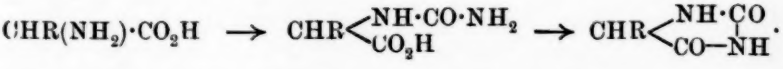
The validity of this assumption was emphasised by the fact that active methylethylhydantoin (III), a compound containing no labile hydrogen atom attached to carbon, and hence incapable of showing keto-enol tautomerism, did not undergo racemisation at all under conditions which would have racemised other hydantoins completely.

It appeared reasonable to ascribe the optical inactivity of the hydantoin derivative, allantoin, to the same cause as that which conditions the racemisation of other hydantoin compounds. The author therefore suggested that allantoin might exhibit tautomeric change of the keto-enol type, the formation of the enol form (V) being followed by loss of asymmetry:

(IV.) (V.)

Recently Titherley (T., 1913, **103**, 1336) has taken exception to this view, and suggested an alternative explanation, which will be referred to later. Titherley writes: "The tautomerism postulated by Mendel and Dakin is improbable, since it requires for its manifestation the influence of negative groups such as are absent in the allantoin molecule. Such keto-enolic tautomerism should, in fact, appear with consequent rapid racemisation in α-amino-acids, and similarly constituted compounds where it is not apparent, if Mendel and Dakin's theory were to be accepted." The author believes that Titherley's criticism cannot be sustained, for in the first place "the influence of negative groups such as are absent in the allantoin molecule" is certainly not necessary for the exhibition of keto-enol tautomerism, neither is the rapid racemisation of α-amino-acids a necessary corollary of our hypothesis, but rather the reverse.

Certain facts will illustrate the above points. The following optically active amino-acids, among others, have been converted successively into the corresponding carbamido-acids and hydantoins: alanine, aspartic acid, glutamic acid, leucine, α-aminophenylacetic acid (Dakin and Dudley, *J. Biol. Chem.*, 1914, **18**, 48), phenylalanine (Dakin and Dudley, *ibid.*, 1913, **17**, 29), and tyrosine:



The parent amino-acids, as is well known, are relatively resistant to racemisation, although prolonged boiling with alkali does effect a slow but perceptible racemisation as with most other com-

pounds*; on treating the active amino-acid with potassium cyanate, the active carbamido-acid is readily obtained without racemisation, and the optical stability of the product is about as great as that of the parent amino-acid. As soon as the active carbamido-acid is converted into the cyclic hydantoin by warming with dilute mineral acids, the optical stability of the product is at once impaired. In the first place, it appears that the actual conversion into hydantoin by acids is usually accompanied by some racemisation, so that the optical rotations for various active hydantoins described by the author can only be regarded as minimum values. In the case of the conversion of 1-α-carbamidophenylacetic acid ($[\alpha]_D$ −133·5°) into phenylhydantoin by boiling with 5 per cent. hydrochloric acid, the product was completely racemised, and the same tendency, but to a less degree, has been observed in several other cases. The activity of the hydantoins was in every case abolished by short treatment with dilute alkali, and the change proceeds rapidly to completion at room temperature. The hydantoins must be regarded as optically unstable compounds whenever their structure permits of keto-enol tautomerism.

The author considers that the assumption that allantoin would exhibit the behaviour common to other hydantoins appears well based, and that at present there is no evidence antagonistic to the idea that these compounds undergo keto-enol tautomeric change.

Titherley suggests that the inactivity of allantoin may be due to tautomerism of a different kind, and assumes the formation of a symmetrical bicyclic structure, the formula for which had been previously considered and rejected on chemical grounds by Biltz (*Ber.*, 1910, **43**, 1999)†:

The occurrence of tautomerism of this character is somewhat

* It appears not improbable that keto-enol tautomerism may be responsible for this change, especially as Dudley and the author have shown that minute amounts of alkylglyoxalbisnitrophenylhydrazones result from the digestion of α-amino- and α-hydroxy-acids with *p*-nitrophenylhydrazine. From a quantitative point of view, the reaction takes place only to a very slight extent (compare footnote, *T.*, 1914, **105**, 2453).

† The only direct evidence in favour of this symmetrical formula is the fact that allantoin may be reduced to the bicyclic glycouril, as shown by Rheineck and confirmed by Biltz. This reaction can be equally well accounted for by the conventional formula for allantoin, and, moreover, the significance of the reaction is lessened by the fact that Biltz has shown that 3-methylallantoin, which is undoubtedly structurally similar to allantoin, on similar reduction yields carbamide and probably methylallantoin. It has not been possible to reconvert glycouril into allantoin, so that on the whole there seems no good reason at present for reconsidering the bicyclic formula for allantoin.

analogous to the tautomerism observed by Titherley in the case of the *O*-acyl and *N*-acyl derivatives of salicylamide, but so far as the author is aware has not been observed in any compounds even remotely related to allantoin.

Since tautomerism of the type suggested by Titherley, as well as that put forward by Mendel and the author, may occur in the case of allantoin, it appeared desirable if possible to submit the question to the test of a crucial experiment. With this end in view, the author has made a large number of attempts to resolve 3-methylallantoin (*β*-methylallantoin) and homoallantoin (pyruvil) into active components, but all have been unsuccessful.

Experimental.

3-Methylallantoin was prepared according to Fischer and Ach's direction (*Ber.*, 1899, **32**, 2746) by the oxidation of 7-methyluric acid with lead peroxide. The latter substance was obtained by the reduction with tin and hydrochloric acid of 7-hydroxymethyluric acid prepared by the action of formaldehyde on sodium urate, as described by Grohmann (*Annalen*, 1911, **382**, 66). The yields throughout were satisfactory.

Homoallantoin was readily prepared according to Simon's method (*Compt. rend.*, 1901, **133**, 587) by heating homoallantoic acid, prepared by the action at room temperature of pyruvic acid on carbamide, with a small amount of water at 100°.*

Three types of experiments were made with each compound in the attempt to effect their resolution into active components.

(*a*) The substances were administered to rabbits, and the unchanged allantoin was isolated from the urine. Portions of a gram, each dissolved in warm water, were given by stomach tube twice a day. The unchanged allantoins were separated from the urine by direct crystallisation after successive treatment with lead acetate and hydrogen sulphide. The yield of substance recovered in each case amounted to about a quarter of that given, and was optically inactive. The substances were not toxic.

(*b*) Ehrlich's method (*Biochem. Zeitsch.*, 1914, **63**, 379) for the

* It is worthy of note that a solution of mercuric acetate with an excess of sodium acetate, such as Wiechowski uses for the quantitative precipitation of allantoin, produces no precipitate with solution of 3-methylallantoin. This fact is probably connected with Biltz's observation that the silver salt of allantoin on methylation yields 3-methylallantoin. It appears probable, therefore, that the mercury complex in Wiechowski's allantoin compound is attached to the nitrogen atom in position 3.

Homoallantoin, as expected, is precipitated by Wiechowski's reagent much in the same way as is allantoin, since the nitrogen in position 3 of homoallantoin is unsubstituted.

resolution of amino-acids by the use of actively fermenting yeast was employed without success. Ten grams of homoallantoin or 3-methylallantoin and 400 grams of sucrose were fermented at room temperature for four days with 200 grams of freshly-washed and pressed yeast. The yeast was removed by filtering through a Berkefeld filter and the sugar-free filtrate concentrated by distillation under diminished pressure, when 5—7 grams of each substance were recovered. The products were entirely inactive.

(*c*) Attempts to resolve the substances by the action of bacteria and moulds were made by growing the organisms in a suitable inorganic salt solution with 0·5 per cent. of the allantoin derivatives, both with and without the addition of 1 per cent. of sucrose. An actively growing organism isolated from urine undergoing ammoniacal fermentation was chosen for some experiments, since it was thought that a urea-decomposing organism might be specially adapted for the decomposition of the ureides under examination. Other experiments were made with mixed organisms obtained from fæces, since allantoin has been shown by Givens (*J. Biol. Chem.*, 1914, **18**, 417) to be readily decomposed by intestinal organisms. In addition, experiments were made with various types of moulds. The organisms grew well, but the recovered allantoins were inactive.

Attempts to prepare optically active homoallantoin from active methylhydantoin were unsuccessful. The action of bromine and carbamide on methylhydantoin under similar conditions to those described by Siemonsen (*Annalen*, 1904, **333**, 101) for the synthesis of allantoin gave negative results. Attempts to reduce Franchimont and Klobbie's nitromethylhydantoin (*Rec. trav. chim.*, 1888, **7**, 13) to aminohydantoin and then to convert the latter into hydantoin by means of potassium cyanate were equally fruitless.

In the course of these experiments some new data were obtained relating to the α-carbamidopropionic acids and methylhydantoins. The active substances have not been previously prepared.

l-α-*Carbamidopropionic Acid*, $CH_3 \cdot CH(NH \cdot CO \cdot NH_2) \cdot CO_2H$.—Optically pure *d*-alanine (5 grams) and potassium cyanate (10 grams) were heated on the water-bath in an open dish with 20 c.c. of water for one hour. The concentrated solution was made just acid to Congo-red with hydrochloric acid. The carbamido-acid crystallised out in good yield, and after recrystallisation from water the melting point was constant. The pure substance is readily soluble in hot water, but requires about seventy parts of cold water for solution. It crystallises in clear, hexagonal prisms, sintering at 195° and melting at 198—200°. (Found, N = 21·0. $C_4H_8O_3N_2$ requires N = 21·2 per cent.)

The rotation was observed in aqueous solution:

$c=1{\cdot}281$; $l=2{\cdot}2$ dm.; $\alpha-0{\cdot}27°$; $[\alpha]_D^{20}-9{\cdot}6°$.

Another preparation under similar conditions gave $[\alpha]_D-9{\cdot}4°$.

l-*Methylhydantoin*, $CH_3{\cdot}CH<\begin{matrix}NH{\cdot}CO\\ CO{-}NH\end{matrix}$.—On boiling *l*-α-carbamidopropionic acid (3 grams) with 50 c.c. of water and 9 c.c. of concentrated hydrochloric acid for two hours, the hydantoin is readily obtained. It is very readily soluble in water, and is left as a crystalline meal on evaporation of the acid. After recrystallisation from a little water, the substance melts at 175—177° without decomposition.

Found: N = 24·7.

$C_4H_6O_2N_2$ requires N = 24·6 per cent.

The substance is strongly lævorotatory in aqueous solution. The actual rotation calculated was $[\alpha]_D^{20}-50{\cdot}6°$ for a 2·836 per cent. solution in water. This can only be regarded as a minimum value, since racemisation is apt to accompany the formation of the hydantoin. The active methylhydantoin is rapidly racemised by digestion with dilute alkali at room temperature.

Inactive α-Carbamidopropionic Acid.—This substance was prepared as described for the active compound. It has a great tendency to form supersaturated solutions, so that recrystallisation is sometimes difficult. After three crystallisations from water the substance sinters slightly at 182°, and melts sharply at 185°. (Found, N = 21·2. Calc., N = 21·2 per cent.) Apart from the melting point, which has been given as 155°, the properties of the substance agree with those described by Urech (*Annalen*, 1873, **165**, 99) and by Heintz (*Annalen*, 1873, **169**, 120). The cause of the discrepancy in the melting-point observations is obscure, but it is possible that the preparations of Urech and Heintz had undergone partial conversion into methylhydantoin.

Inactive α-Methylhydantoin.—The substance was prepared in the same way as the active compound. It may be extracted by ether from its aqueous solution in a few hours in a continuous extractor. It crystallises in clear, hard prisms, melting sharply at 150° without decomposition. The melting point of the substance is stated to be 125° and 140° by Urech and by Heintz respectively. The other properties observed agree with the earlier descriptions. On boiling with dilute barium hydroxide and then removing the barium quantitatively with sulphuric acid, the hydantoin was re-converted into α-carbamidopropionic acid, which crystallised out on concentrating the solution, and melted at 185°.

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NEW YORK.

[*Received February 23rd*, 1915.]

LI.—*Conversion of Racemic Acid into a Mixture of Racemic and* d-*Tartaric Acids by Means of* l-*Malic Acid.*

By Alex. McKenzie.

According to Pasteur, ammonium hydrogen *d*-tartrate combines with ammonium hydrogen *l*-malate to form a crystalline compound, which, when dissolved in aqueous ammonia, has the same rotatory power as is possessed by a mixture of equimolecular quantities of the two salts.

This statement led the author to attempt the resolution of optically inactive acids by combining them with active acids instead of with the active bases which are usually employed for the purpose. On the basis of Pasteur's observation, if ammonium hydrogen racemate were combined with ammonium hydrogen *l*-malate, two compounds would probably be produced, namely, (*a*) ammonium hydrogen *d*-tartrate + ammonium hydrogen *l*-malate (Pasteur's salt), and (*b*) ammonium hydrogen *l*-tartrate + ammonium hydrogen *l*-malate. Since complexes of this nature are not enantiomorphously related, their separation might be effected in virtue of the difference in solubility, which would doubtless exist between them. In this connexion the remark of Pasteur that the ammonium hydrogen salt of *l*-tartaric acid does not form a compound with the ammonium hydrogen salt of *l*-malic acid is significant, indicating, as it does, that salt (*b*) is more soluble in water than salt (*a*).

In the course of an investigation of this problem the unexpected results, which are described in the present paper, were encountered.

Racemic acid (1 mol.) was neutralised with aqueous potassium hydroxide, and *l*-malic acid (1 mol.) was added. The crystalline product which separated was dextrorotatory, and consisted of a mixture of potassium hydrogen racemate and potassium hydrogen *d*-tartrate.

Now the addition of a nucleus of an optically active compound to a solution of the inactive form is known in certain cases to cause the deposition of optically active crystals. Gernez, for example, found that, when a nucleus of sodium ammonium *d*-tartrate is added to a supersaturated solution of sodium ammonium racemate, the resulting crystals consist of the *d*-salt, whereas, when a nucleus of the *l*-tartrate is added, the *l*-salt separates (*Compt. rend.*, 1866, **63**, 843). Other cases of this extension of Pasteur's original method of mechanical separation are afforded in the resolution of zinc ammonium lactate (Purdie, T., 1893, **63**, 1143) and of

the phenylbenzylhydrazones of erythrose (Ruff, *Ber.*, 1901, **34**, 1362). Moreover, Ostromisslenski (*Ber.*, 1908, **41**, 3035) has shown that *l*-asparagine causes the crystallisation of sodium ammonium *d*-tartrate when a nucleus of it is added to a supersaturated solution of the racemate, whilst Kipping and Pope (*T.*, 1909, **95**, 103), in a series of experiments on the crystallisation of externally compensated mixtures, have shown that nuclei present in the dust of the atmosphere of the laboratory induce crystallisation in a solution of sodium ammonium racemate, the crystals formed being sometimes dextrorotatory and sometimes lævorotatory.

The most probable explanation of the activation of racemic acid by malic acid would naturally be sought for on these lines. The phenomenon must, however, be ascribed to some other cause. In no case has potassium hydrogen racemate been crystallised from water alone so as to cause the deposition of an optically active salt.

One other observation may be recorded at the present time. Van't Hoff has suggested the possibility of activating an inactive compound by crystallising it from an optically active solvent. This idea has now been experimentally realised in the following manner. When potassium hydrogen racemate is crystallised from an aqueous solution of *l*-malic acid, the crystals which separate are dextrorotatory, and consist of a mixture of potassium hydrogen racemate and potassium hydrogen *d*-tartrate.

Experimental.

The racemic acid used in each case was tested to make certain that it was optically inactive. No optical activity was detected with a concentrated aqueous solution. Two grams of the acid were dissolved in water and neutralised by potassium hydroxide; the whole of the solution was polarimetrically examined in a 2-dcm. tube, and found to be inactive.

Experiment I.—A solution of 10 grams of racemic acid (1 mol.) in water was neutralised by the calculated quantity of potassium hydroxide, and made up to 500 c.c. Eight grams of *l*-malic acid (1 mol.) were then dissolved in the solution of potassium racemate which had previously been warmed, and crystals began to separate before the liquid was cold. The whole was then stirred vigorously, and allowed to remain for two days at the ordinary temperature. The crystals were collected, washed with 10 c.c. of water, dried on porous plate, and then at 100° for one hour. The yield was 11 grams (crop A).

0·2394 required 47·25 c.c. of baryta ($N/40 \times 1{\cdot}077$) for neutralisation, whereas $CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2K$ requires 47·26 c.c.

Two grams of A were neutralised by potassium hydroxide and made up to the bulk necessary to fill a 1-dcm. tube (8·1 c.c.). *The solution was distinctly dextrorotatory*, giving $\alpha_D + 0{\cdot}44°$. Eleven c.c. of *N*-sulphuric acid were then added, and the resulting salt (1·8 grams) was collected and crystallised from 100 c.c. of water. The crystals which separated amounted to 1·4 grams. They were neutralised, and the solution of the potassium salt examined in a 1-dcm. tube. The dextrorotation was still slight but definite ($+0{\cdot}08°$) after this treatment.

Since the addition of boric acid to *d*-tartaric acid is known to enhance the rotatory power of the latter, a mixture of 2 grams of A and 1·5 grams of boric acid was heated with water, and the solution examined in a 2-dcm. tube. The value $\alpha_D + 1{\cdot}34°$ was observed.

Experiment II.—Ten grams of racemic acid were neutralised and acted on with *l*-malic acid as before. After twenty-four hours the crystals (crop B) amounted to 9·5 grams.

6·5 Grams of B were neutralised by potassium hydroxide, and the solution was examined in a 2-dcm. tube. Found, $\alpha_D + 1{\cdot}3°$.

Since ordinary tartar emetic is strongly dextrorotatory, a mixture of 2·9 grams of B and 2·2 grams of antimony oxide were made into a paste with water and heated on the water-bath for half-an-hour, water being added at intervals. The product was then boiled with water and filtered. After being kept overnight, the crystals amounted to 3·3 grams, whilst the filtrate gave $\alpha_D + 5{\cdot}4°$ in a 2-dcm. tube.

Experiment III.—100 C.c. of an aqueous solution of potassium racemate, prepared from 5 grams of racemic acid, were heated at 80°, and 4 grams of *l*-malic acid were added. The product (C) amounted to 5·5 grams:

0·693 (dried at 130°) gave 0·3188 K_2SO_4. K = 20·6.

$C_4H_5O_6K$ requires K = 20·7 per cent.

One gram of C was neutralised by potassium hydroxide, and the solution made up to 20 c.c. The observed value was $\alpha_D + 0{\cdot}22°$ ($l = 2$), and this corresponds with $[\alpha]_D + 1{\cdot}8°$ when referred to the normal potassium salt, whereas potassium *d*-tartrate has, according to Landolt, $[\alpha]_D + 27{\cdot}39°$.

The filtrate, from which C had been removed, amounted to 90 c.c., a portion of it in a 2-dcm. tube giving $\alpha_D - 0{\cdot}82°$.

3·8 Grams of C were dissolved by boiling with 100 c.c. of water. The crystals which separated overnight were neutralised as usual, and the solution was made up to 20 c.c., a portion of which in a 2-dcm. tube gave $\alpha_D + 0{\cdot}34°$; the filtrate from which the crystals had been removed was also dextrorotatory.

Experiment IV.—2·3 Grams of racemic acid (1 mol.) were neutralised and made up to 100 c.c. 3·8 Grams of *l*-malic acid (2 mols.) were added. The crystals (2·5 grams) were treated as in experiment I. Found, α_D +0·5°.

Experiment V.—1·6 Grams of *l*-malic acid were neutralised, and 2 grams of racemic acid were added to the solution. Volume = 100 c.c. Crystals = 2 grams; treated as in experiment I; found, α_D +0·44°.

Crystallisation of Potassium Hydrogen Racemate from an Aqueous Solution of l-*Malic Acid.*

Racemic acid was neutralised by aqueous potassium hydroxide and the acid salt was precipitated by the addition of sulphuric acid. The salt was crystallised from water; the potassium salt, obtained from the recrystallised acid salt, was optically inactive.

A solution of 3·2 grams of *l*-malic acid (1 mol.) in 210 c.c. of water was heated to boiling, and 4·4 grams of recrystallised potassium hydrogen racemate (1 mol.) were added. The solution was boiled for five minutes, and the clear solution then poured into a beaker and stirred. After twenty-four hours, the crystals, which had separated, were collected (filtrate = 190 c.c.), washed with 10 c.c. of water, and dried at 100° for one hour. Yield, 3·2 grams:

0·2784 required 55 c.c. of baryta ($N/40 \times 1{\cdot}077$) for neutralisation. $CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2K$ requires 54·96 c.c.

2·844 Grams of the salt were neutralised by the calculated quantity of potassium hydroxide, and the solution was made up to 16 c.c., the bulk necessary to fill a 2-dcm. tube. *The solution was distinctly dextrorotatory*, giving α_D +0·39°. It was then made up to 50 c.c., and the salt was precipitated by the addition of 16 c.c. of *N*-sulphuric acid. After three hours' keeping, the filtrate was treated with 16 c.c .of *N*-sulphuric acid, and evaporated to the bulk necessary to fill a 1-dcm. tube; the solution was slightly dextrorotatory, giving α_D +0·09°. The crystals were crystallised from 100 c.c. of boiling water. The product (1·9 grams) was dissolved in potassium hydroxide, and then gave α_D +0·08° in a 2-dcm. tube.

This work is being continued.

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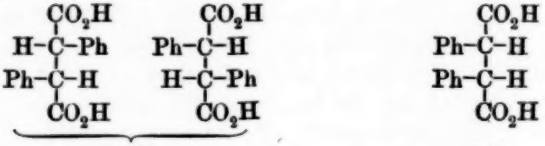
[*Received March 15th*, 1915].

LII.—*Configuration of the Stereoisomeric Diphenylsuccinic Acids.*

By Henry Wren and Charles James Still.

In spite of the large amount of research which has been devoted to the symmetric diphenylsuccinic acids, the question of their configuration has not been definitely settled. Since these substances contain two asymmetric carbon atoms, each united to the same groups, it is obvious that one of them (i) must be resolvable into optically active components, whilst the other (ii) must be of the *meso* type:



(I.) (II.)

In the present communication it is shown that β-diphenylsuccinic acid is to be regarded as *meso*diphenylsuccinic acid and α-diphenylsuccinic acid as *r*-diphenylsuccinic acid. The resolution of the latter was accomplished by the use of brucine in aqueous solution, the brucine salt of the *d*-acid being the more sparingly soluble. d-*Diphenylsuccinic acid* melts to a pasty, non-transparent liquid at 179—180° after previous slight shrinkage, then re-solidifies, and again melts at 212—214° to a yellow liquid, from which gas is not evolved. It has $[\alpha]_D^{14}$ +397·9° when dissolved in acetone and $[\alpha]_D^{16\cdot5}$ +369·7° in ethyl-alcoholic solution. l-*Diphenylsuccinic acid* melts at 176—177°, re-solidifies, and again melts at 211·5—214°. In ethyl-alcoholic solution it has $[\alpha]_D^{13}$ −368·9°. *d*-Diphenylsuccinic acid has been isolated in an almost pure condition by McKenzie, Drew, and Martin (T., 1915, **107**, 32) from the products of the action of magnesium phenyl bromide on *l*-phenylchloroacetic acid. The specimen which they obtained had $[\alpha]_D^{15}$ +348° in ethyl-alcoholic solution, and, after being dried at 100°, shrank sharply to a thin core at 170—171°, which was unchanged until 211·5°, when it melted sharply to a clear liquid, from which gas was not evolved.

A consideration of the relative stability of the anhydrides of α- and β-diphenylsuccinic acids has led Anschütz and Bendix (*Annalen*, 1890, **259**, 81) to the conclusion that the α-acid is the racemic variety.

α-Diphenylsuccinic acid has a lower melting point than the β-acid, and is the resolvable form. In the case of the isomeric dibromo-

succinic acids, McKenzie (T., 1912, **101**, 1196) has shown that it is the *iso*-form which melts at a lower temperature than its inactive isomeride, and can be resolved into optically active components, whilst Werner and Basyrin (*Ber.*, 1913, **46**, 3229) found that the dimethylsuccinic acid of lower melting point is the resolvable form. The case of the $\alpha\alpha'$-dimethyladipic acids, investigated by Noyes and Kyriakides (*J. Amer. Chem. Soc.*, 1910, **32**, 1057), presents similar features. It appears remarkable that, in the instances of the symmetric di-substituted succinic acids which have been examined from this point of view, the isomeride of lower melting point should be the racemic acid, whilst in the tartaric acid group the reverse is the case.

Experimental.

Interaction of Ethyl Phenylacetate and Iodine in Dry Ethereal Solution in the Presence of Solid Sodium Ethoxide.

α-Diphenylsuccinic acid was prepared by Franchimont (*Ber.*, 1872, **5**, 1050) by the action of an alcoholic solution of potassium cyanide on ethyl phenylbromoacetate and treatment of the product with potassium hydroxide. Subsequently, Reimer (*Ber.*, 1881, **14**, 1802) found that this acid, and also the β-acid, are obtained by reducing the anhydride of stilbenedicarboxylic acid by means of sodium amalgam in dilute alkaline solution, and that they can be conveniently separated by taking advantage of the widely differing solubilities of the respective barium salts in water. According to Anschütz and Bendix (*loc. cit.*), the barium salt of the α-acid is soluble in 312 parts of water at 17—18°, whilst the corresponding salt of the β-acid requires only 4·742 parts of water for solution. Reimer also showed that the α-acid is completely converted into the β-isomeride by protracted treatment with aqueous hydrochloric acid at 200°, whilst the reverse transformation may be effected by the use of an excess of aqueous barium hydroxide at the same temperature. It was further found that the hydrolysis of diphenylsuccinonitrile at 200° by means of aqueous hydrochloric acid leads to the formation of β-diphenylsuccinic acid, and this method gains additional value from the observation of Chalanay and Knoevenagel (*Ber.*, 1892, **25**, 285) that the nitrile can be prepared in quantity by heating an equimolecular mixture of phenylacetonitrile and mandelonitrile in alcoholic solution in the presence of solid potassium cyanide at 50—60° during twelve to eighteen hours. In the course of the present investigation, considerable amounts of the β-acid have been prepared in this manner, but the inconvenience of obtaining the requisite quantity of acids by methods involving the use of sealed tubes has led to the investigation of

other processes. It has been found by Komnenos (*Annalen*, 1910, **375**, 254) that small yields of ethyl β-diphenylsuccinate are obtained when an ethereal solution of iodine is added to a moderately dilute alcoholic solution of ethyl phenylacetate and sodium ethoxide. By diminishing the quantity of alcohol employed, however, the amount of ester obtained can be considerably increased, but a more decided improvement is effected by performing the condensation in dry ethereal solution in the presence of solid sodium ethoxide; in these circumstances, ethyl β-diphenylsuccinate is readily isolated, whilst, in addition, notable amounts of ethyl α-diphenylsuccinate are obtained. The following experiment is typical.

A solution of iodine (27·3 grams) in absolute ether (140 c.c.) was gradually added to a well-cooled mixture of ethyl phenylacetate (35 grams), ether (70 c.c.), and finely powdered sodium ethoxide obtained from 5·7 grams of sodium. The colour of the iodine disappeared instantly, and a white precipitate was formed, which, when preserved, became yellow and ultimately yellowish-brown. The product of the reaction was treated with water and sodium thiosulphate solution, when an almost colourless aqueous layer and a yellow ethereal solution were obtained, between which a considerable quantity of a yellowish precipitate (*A*) was suspended. The latter was separated, the aqueous layer was extracted with ether, and the combined ethereal solutions were dehydrated over anhydrous sodium sulphate. After the removal of the ether, the residue was heated under diminished pressure, whereby unchanged ethyl phenylacetate (3·2 grams), strongly coloured with iodine, was recovered. The residual ester solidified to a brownish-yellow cake (*B*).

The solution of the precipitate (*A*) in boiling alcohol deposited, on cooling, ethyl β-diphenylsuccinate (9·7 grams), m. p. 139—140°. The mother liquor was used for the crystallisation of the cake (*B*), whereby a mixture of the α- and β-esters (8 grams), m. p. 74—130°, was isolated; the filtrate was evaporated to dryness, and the residue was treated with sodium thiosulphate to remove further quantities of iodine which had gradually separated,* and crystallised from light petroleum (b. p. 40—60°), when a quantity of approximately pure α-ester, contaminated with a small amount of resinous matter, was obtained. The separation of the isomeric esters was accom-

* In the course of these condensations, an unstable iodine compound, possibly ethyl phenyliodoacetate, is formed from which iodine is not completely eliminated by the aid of sodium thiosulphite or by heating at about 140° under diminished pressure. The separation of the halogen appears to be greatly facilitated by exposure to bright light. Somewhat analogous observations have been made by McKenzie, Drew and Martin (*loc. cit.*).

panied by considerable loss, and was best effected by repeated extraction of the mixture with successive small quantities of boiling light petroleum (b. p. 40—60°), in which the β-ester is sparingly soluble. The final purification of the α-ester was accomplished by several crystallisations from methyl alcohol, and subsequently from light petroleum. In this manner 3·2 grams of pure α-ester were obtained from the above mixture, in addition to a further quantity (2·1 grams) of β-ester.

Ethyl β-diphenylsuccinate separates from ethyl alcohol in almost colourless needles, which melt at 140—141° (corr.), whereas Reimer (*loc. cit.*) gives 136°, Anschütz and Bendix (*loc. cit.*) 140—141°, and Komnenos (*loc. cit.*) 140°. (Found, C=73·7; H=6·9. Calc., C=73·6; H=6·8 per cent.)

Ethyl α-diphenylsuccinate melts at 82—83·5° (corr.). The values recorded are 84—85° (Reimer) and 84° (Anschütz and Bendix). (Found, C=73·9; H=6·9. Calc., C=73·6; H=6·8 per cent.)

Action of Acids and Alkalis on the Isomeric Ethyl Diphenylsuccinates.

Ethyl β-diphenylsuccinate is hydrolysed when heated in a sealed tube with concentrated aqueous hydrochloric acid at 200° during five and a-half hours, β-diphenylsuccinic acid being produced in good yield. Considerable discrepancies are shown in the melting points observed for this substance, the following data being recorded: 229°, Reimer (*loc. cit.*); 229—230°, Chalanay and Knoevenagel (*loc. cit.*); 245°, Anschütz and Bendix (*loc. cit.*); 252°, with evolution of gas on rapid heating, Roser (*Annalen*, 1888, **247**, 152); 252°, Ruhemann and Naunton (T., 1912, **101**, 50); 228—230°, McKenzie, Drew, and Martin (*loc. cit.*). The acid obtained by the method described above, as well as that prepared by the action of hydrochloric acid on diphenylsuccinonitrile, was found to melt at 229—230°, and this value remained unchanged after repeated crystallisation from ethyl or amyl alcohol or from ethyl benzoate.

The fact that β-diphenylsuccinic acid can be completely converted into the α-isomeride by protracted treatment with an excess of aqueous barium hydroxide at a somewhat elevated temperature, pointed to the probability that a mixture of the potassium salts of the α- and β-acids would be obtained by the hydrolysis of ethyl β-diphenylsuccinate by potassium hydroxide. This hypothesis was confirmed by an experiment in which ethyl β-diphenylsuccinate (4 grams) was heated with a solution of potassium hydroxide (1·9 grams) in ethyl alcohol (30 c.c.) and water (10 c.c.). The resulting solution was exactly neutralised with hydrochloric

acid, evaporated to remove alcohol, and treated with a hot aqueous solution of barium chloride. A crystalline precipitate of barium α-diphenylsuccinate was obtained, which weighed 4·3 grams, and from which α-diphenylsuccinic acid was isolated by the addition of hydrochloric acid. The acid melted at 180—181°, re-solidified, and again melted at 220°, whereas Reimer (*loc. cit.*) gives 183° and 222°. The filtrate from the above barium salt yielded β-diphenylsuccinic acid on the addition of mineral acid. In a somewhat similar experiment, Komnenos (*loc. cit.*) found that the acid obtained by the hydrolysis of ethyl β-diphenylsuccinate melted at 160°, and was led to the conclusion that it was probably a mixture of the isomeric acids.

The saponification of ethyl α-diphenylsuccinate with aqueous-alcoholic potassium hydroxide proceeds normally, a good yield of α-diphenylsuccinic acid being obtained on the addition of mineral acid to the product.

Preparation of α-Diphenylsuccinic Acid.

When it is desired to prepare α-diphenylsuccinic acid from the product of the action of iodine and sodium ethoxide on ethyl phenylacetate, the separation of the isomeric diphenylsuccinic esters is unnecessary. The following experiment illustrates the method adopted:

Finely-powdered sodium ethoxide (obtained from 8 grams of sodium) was suspended in a solution of ethyl phenylacetate (49·2 grams) in anhydrous ether (100 c.c.). An ethereal solution of iodine (38·1 grams in 200 c.c.) was slowly added to the mixture, which was cooled by immersion in ice and water. After remaining during some hours at the ordinary temperature, water and sodium thiosulphate solution were added. The flocculent precipitate of ethyl β-diphenylsuccinate was removed, and the aqueous solution extracted with ether. The combined ethereal extracts were dried, and, after the removal of the ether, heated under diminished pressure, whereby unchanged ethyl phenylacetate (7 grams) was recovered. The residue in the distilling flask was united with the precipitated ester and hydrolysed by an excess of aqueous-alcoholic potassium hydroxide. The resulting solution was heated in an open dish until the alcohol was completely removed, filtered from a small amount of brown, resinous matter, heated to boiling, and treated with an excess of a boiling concentrated solution of barium chloride in water, when a heavy, white precipitate of barium α-diphenylsuccinate was obtained. This was filtered and washed with water. The filtrate was transferred to an autoclave, and heated for five hours at 195°, when a further quantity of barium

α-diphenylsuccinate was precipitated, which was removed after exact neutralisation of the excess of alkali by means of hydrochloric acid. The united crops were suspended in water, and decomposed by hydrochloric acid. The precipitated α-diphenylsuccinic acid was crystallised from boiling water, when 18·8 grams of acid were obtained, which melted at 183°, and, after re-solidification, at 220—221°. The yield obtained, calculated on the amount of ethyl phenylacetate which entered into action, was 50·4 per cent. of that theoretically possible.

Resolution of α-Diphenylsuccinic Acid.

A mixture of α-diphenylsuccinic acid (30 grams) and brucine (97·1 grams) was heated on the boiling-water bath with water (6,820 c.c.), until almost complete solution was obtained. After filtration, the solution was allowed to cool, and seeded with a small quantity of brucine α-diphenylsuccinate obtained from a previous resolution. (In this instance, the use of a pure seeding material was found to be without influence on the purity of the crop, but advantageous in that it caused the latter to separate fairly rapidly and in a much more distinctly crystalline condition than was otherwise the case.) After remaining for some days in an ice-chest at about 5°, the crop was separated and dried on porous earthenware, when 87 grams of crystals were obtained, which were purified by repeated crystallisation from hot water, 70 c.c. of the solvent being used for each gram of product. The course of the resolution was followed by dètermining the specific rotation of the acid recovered from the successive filtrates. The following values for $[\alpha]_D$ were thus obtained, the observations being made in acetone solution: −195·2°, −109·6°, +10·1°, +76·6°, +206·7°, +252·9°. The crop from which the last filtrate had been obtained, which consisted of long, well-formed prisms weighing 20·8 grams, was decomposed by treatment with dilute hydrochloric acid, and extracted with ether, whereby 4·5 grams of *d*-diphenylsuccinic acid, having $[\alpha]_D$ +344·9° in acetone solution, were isolated. After two crystallisations of this acid from considerable quantities of water, this value had risen to +397·3°, and then remained unchanged after a further recrystallisation.

d-*Diphenylsuccinic acid* separates from water in felted masses of minute needles. It is sparingly soluble in the hot solvent, very sparingly so in the cold. It dissolves sparingly in boiling benzene, readily in cold ether, methyl and ethyl alcohols, and in ethyl acetate. When heated in a capillary tube, it melts to a pasty liquid at 179—180°, then solidifies, and melts at 212—214° to a yellow liquid, from which gas is not evolved. The temperatures are,

however, somewhat dependent on the mode of heating, and the diameter of the tube employed. The acid is hygroscopic. Analyses and determinations of specific rotation were made with samples which had been dried at 100—105° until constant in weight:

0·1412 gave 0·3688 CO_2 and 0·0666 H_2O. C = 71·2; H = 5·3.
$C_{16}H_{14}O_4$ requires C = 71·1; H = 5·2 per cent.

The following determinations of the specific rotation were made:

In acetone solution:

$l = 2$, $c = 1·4525$, a_D^{17} +11·54°, $[a]_D^{17}$ +397·3°
$l = 2$, $c = 2\ 3015$, a_D^{14} +18·32°, $[a]_D^{14}$ +397·9°.

In ethyl-alcoholic solution:

$l = 2$, $c = 1·4955$, a_D^{15} +11·05°, $[a]_D^{15}$ +369·5°
$l = 2$, $c = 2·3450$, $a_D^{16·5}$ +17 34°, $[a]_D^{16·5}$ +369·7°.

In methyl-alcoholic solution:

$l = 2$, $c = 1·8075$, a_D^{16} +12·61°, $[a]_D^{16}$ +369·2°.

In ethyl acetate solution:

$l = 2$, $c = 1·4665$, a_D^{16} +11·82°, $[a]_D^{16}$ +403·0°.

In another experiment an attempt was made to effect the final purification of the *d*-acid by crystallisation from benzene, but this solvent was found to be less suitable for the purpose than water.

Preparation of l-*Diphenylsuccinic Acid.*

The isolation of *l*-diphenylsuccinic acid was accomplished by the fractional crystallisation from water of the crude, lævorotatory mixture of acids obtained from the filtrate from the first crop of brucine salt (see above). In one case, crude *l*-diphenylsuccinic acid (11 grams, $[a]_D$ −135·2° in ethyl-alcoholic solution) was dissolved in boiling water, 160 c.c. of the latter being used for each gram of acid. A somewhat felted crop separated on cooling, which, after being dried, weighed 5·6 grams, and had $[a]_D$ −259° ($c = 2·6255$) in ethyl-alcoholic solution. On continuing the process, using the same relative quantities of acid and water, the successive crops had $[a]_D$ −347·6°, −361·8°, −366·0°, −368·0°, and −368·9°, the latter value agreeing satisfactorily with the value, +369·7°, found for the *d*-acid in the same solvent.

l-*Diphenylsuccinic acid* closely resembles its *d*-isomeride in its properties. It melts at 176—177° to a pasty liquid, which then resolidifies and again melts at 211·5—214° to a yellow liquid, from which gas is not evolved. As in the case of the *d*-acid, these tem-

peratures depend somewhat on the rate of heating and the diameter of the capillary tube.

For the analysis and for the determination of the specific rotation the acid was dried at 100—105° until constant in weight:

0·1339 gave 0·3473 CO_2 and 0·0632 H_2O. C = 70·7; H = 5·3.

$C_{16}H_{14}O_4$ requires C = 71·1; H = 5·2 per cent.

The specific rotation was determined in ethyl-alcoholic solution:

$l = 2$, $c = 2·3325$, α_D^{13} −17·21°, $[\alpha]_D^{13}$ −368·9°.

The unexpectedly great purification caused by the first crystallisation of the crude *l*-acid, considered in conjunction with the weights of material involved, rendered an examination of the acid contained in the filtrate a matter of interest. It was therefore extracted with ether, and, on examination in ethyl-alcoholic solution, was found to be slightly dextrorotatory ($l = 2$, $c = 4·167$, α_D +0·34°, $[\alpha]_D$ +4·1°). This result was at first attributed to the presence of an optically active impurity in the materials employed, but the initial α-diphenylsuccinic acid was optically inactive, whilst, also, a series of blank experiments gave completely negative results. In a second experiment an acid having $[\alpha]_D$ −152° was crystallised under similar conditions; the acids obtained from the crop and filtrate respectively had $[\alpha]_D$ −295·5° and +3·05° in ethyl-alcoholic solution. In like manner, a crude *d*-acid which had $[\alpha]_D$ +135·6°, was separated into two portions, having $[\alpha]_D$ +255·2° and −3·7° respectively.

Attempts were also made to employ other alkaloids for the resolution of α-diphenylsuccinic acid. With quinine, cinchonine, strychnine, or morphine in aqueous solution, and with morphine in ethyl-alcoholic solution, no evidence of resolution could be obtained.

Attempts to Resolve β-Diphenylsuccinic Acid.

In the preliminary part of this investigation attempts were made to resolve β-diphenylsuccinic acid by means of morphine and brucine respectively in aqueous solution. In each case, crystalline salts were readily prepared, from which, however, an optically active acid was not obtained; these salts were not further investigated.

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[*Received March 3rd*, 1915].

LIII.—*Studies in Phototropy and Thermotropy. Part VI. Polymorphic Vanillylidenearylamines Produced by Trituration and by the Influence of Actinic Light.*

By Alfred Senier and Robert Benjamin Forster.

This communication is a record of further search for compounds exhibiting phototropy or thermotropy. The compounds studied are the polymorphic varieties produced by trituration of substituted *p*-hydroxybenzylidenearylamines.

That trituration or rubbing is capable of producing polymorphic change in inorganic compounds, as, for example, in the case of mercuric iodide, has long been known. The first mention of a corresponding effect among organic compounds appears to be that by Piutti (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 635) in the case of certain maleic and fumaric derivatives of *p*-aminophenol. In 1909 Senier and Shepheard (T., 1909, **95**, 1951, 1954) pointed out that this phenomenon is exhibited by *p*-hydroxybenzylidene-*m*-toluidine and by vanillylidene-*m*-toluidine (*p*-hydroxy-*m*-methoxybenzylidene-*m*-toluidine). In a recent paper (T., 1914, **105**, 2462) we showed that this polymorphic change is a general character of *p*-hydroxybenzylidenearylamines, and the present communication proves that it is equally a general property of their vanillylidene analogues; the presence of the *m*-methoxyl group has no inhibiting influence.

It was noticed that "the deeper coloured varieties" on keeping gradually revert to the corresponding "paler coloured varieties." This change takes place when they are removed from the influence of actinic light to avoid possible interference of phototropy for periods, in some cases of a few hours, in others of a few months.

Most of the bases exhibit thermotropy within certain limits of temperature. The term "the lower temperature" is used as in previous papers to denote that attained by immersion in solid carbon dioxide. The thermotropic colour changes on lowering the temperature in all previous instances have been from a deeper to a paler colour, but several of the substances studied in this paper show a reverse thermotropic colour change. No phototropy was detected among these bases or their polymorphic varieties, although by prolonged exposure to sunlight for periods of three or four months most of the compounds became much deeper in colour. These deeper coloured substances are described as polymorphic forms; but it may well be that they are really phototropic varie-

ties, for the reverse change may be expected to require removal from the influence of actinic light for a period of many months, or even years. We have instituted experiments to endeavour to determine this point. The polymorphic varieties obtained by trituration generally show a deeper change of colour on prolonged exposure to actinic light than that exhibited by the original bases.

All the bases described were examined for triboluminescence, but none was observed.

The bases were prepared in the same manner as those described in our last paper (*loc. cit.*). They dissolve in the usual organic solvents; the only notable exception is vanillylidenebenzidine, which is almost insoluble in all but nitrobenzene. Great care was exercised in noting differences of colour to ensure that the conditions of comparison were equal, and any personal error was eliminated by the independent inspection of other observers.

Vanillylideneaniline, $OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N{\cdot}C_6H_5$, was first prepared by Ott (*Monatsh.*, 1905, **26**, 335), who found it to melt at 152—153°. Our specimen, crystallised from light petroleum, melts at 157° (corr.). The needles which first separate from a hot solution in light petroleum are bright yellow, but become pale yellow within a few minutes.

Trituration produces no apparent change. The crystals obtained from different solvents have the same colour. The base is not affected by actinic light, but is thermotropic between "the lower temperature" and about 150°.

Vanillylidenetoluidines, $OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N{\cdot}C_6H_4Me$.

Vanillylidene-*o*-toluidine (Manchot and Furlong, *Ber.*, 1909, **42**, 4388) consists of biscuit-coloured plates, which, after being crystallised from light petroleum, melt at 113—114° (corr.), (115·5° M. and F.). No polymorphic change was detected either by trituration or by the influence of different solvents, and the compound is unaltered by actinic light. It exhibits thermotropy, however, between the ordinary temperature and 90°.

The specimen of vanillylidene-*m*-toluidine (Senier and Shepheard, T., 1909, **95**, 1954), which was crystallised from a mixture of chloroform and light petroleum, is very pale yellow, and melts at 84° (corr.). It is dimorphous (*loc. cit.*). Trituration changes it to a canary-yellow variety. Contrary to our previous experience (*loc. cit.*), we now find that *the paler coloured variety* of the compound is thermotropic between "the lower temperature" and about 80°. *The deeper coloured variety*, on being kept in the dark for a week, changes to the original variety. Thermotropy was observed between "the lower temperature" and the ordinary

temperature. At about 50° this variety reverts to the original paler coloured variety. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-*p*-toluidine (Manchot and Furlong, *Ber.*, 1909, **42**, 4388) consists of very pale yellow needles; it was crystallised from light petroleum, and melts at 119—120° (corr.) (117°, M. and F.). It is dimorphous; by trituration a slightly deeper coloured, polymorphic variety is obtained. *The paler coloured variety* is thermotropic between "the lower temperature" and about 100°. On quickly cooling a hot solution in light petroleum, the deep yellow crystals which separate exhibit thermotropy by rapidly becoming pale yellow as the temperature becomes lower. *The deeper coloured variety* is not thermotropic, but at about 50° reverts to the paler variety. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidenexylidines, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_3Me_2$.

Vanillylidene-o-4-*xylidine* crystallises from a mixture of chloroform and light petroleum in very pale yellow needles, which melt at 112—113° (corr.):

0·1551 gave 7·4 c.c. N_2 at 17° and 744 mm. N = 5·50.

$C_{16}H_{17}O_2N$ requires N = 5·48 per cent.

Vanillylidene-*o*-4-xylidine is dimorphous; a deep yellow variety is produced by trituration. *The paler coloured variety* is thermotropic between "the lower temperature" and about 100°. This compound, and some others described in this paper, change on cooling below the ordinary temperature to a darker thermotropic modification, not to a lighter, as in all previous instances studied. *The deeper coloured variety* is thermotropic at "the lower temperature," and at 100° reverts to the original form. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-m-4-*xylidine* crystallises from light petroleum in colourless plates, which quickly become brownish-yellow in sunlight. It melts at 109° (corr.):

0·2378 gave 11·0 c.c. N_2 at 19° and 746 mm. N = 5·31.

$C_{16}H_{17}O_2N$ requires N = 5·48 per cent.

Vanillylidene-*m*-4-xylidine is not changed by trituration. It is not phototropic, but is converted into a *polymorphic form* of a deeper tint of brown on prolonged exposure to light. The

brownish-yellow colour assumed by the crystals after separating from the solvent is doubtless due to partial polymorphic change. It exhibits thermotropy between "the lower temperature" and the ordinary temperature. The colour at the lower temperature is deeper than that at the ordinary temperature.

Vanillylidene-p-xylidine crystallises from xylene in very pale yellow needles, which melt at 103° (corr.):

0·1718 gave 8·2 c.c. N_2 at 15° and 754 mm. N = 5·61.
$C_{16}H_{17}O_2N$ requires N = 5·48 per cent.

Vanillylidene-*p*-xylidine is dimorphous; on trituration its colour becomes slightly deeper yellow. *The paler coloured variety* is not affected by light. It is thermotropic between "the lower temperature" and 100°. *The deeper coloured variety* is not phototropic, but on very long exposure to sunlight gives slight indications of change to a *polymorphic form*. This variety is not thermotropic, but at 90° reverts to the original paler coloured variety.

Vanillylidene-ψ-cumidine, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_2Me_3$, crystallises from light petroleum in very pale yellow needles, which melt at 123—124° (corr.):

0·1990 gave 9·7 c.c. N_2 at 21° and 751 mm. N = 5·60.
$C_{17}H_{19}O_2N$ requires N = 5·21 per cent.

Vanillylidene-ψ-cumidine is dimorphous. On crushing the crystals, a colourless powder is obtained, which on trituration becomes pale greenish-yellow. *The paler coloured variety* is not phototropic, but on prolonged exposure a biscuit-coloured, apparently permanent, *polymorphic form* is obtained. This variety is thermotropic between "the lower temperature" and about 110°. At temperatures below the ordinary temperature the colour becomes deeper. *The deeper coloured variety* is not affected by actinic light. It is thermotropic between "the lower temperature" and the ordinary temperature, and reverts to the paler coloured variety at about 70°.

Vanillylidene-p-chloroaniline, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Cl$, crystallises from benzene in nearly colourless prisms, which melt at 128—129° (corr.):

0·2123 gave 9·6 c.c. N_2 at 16° and 763 mm. N = 5·36.
$C_{14}H_{12}O_2NCl$ requires N = 5·35 per cent.

Vanillylidene-*p*-chloroaniline is dimorphous. On trituration, the compound becomes pale yellow. *The paler coloured variety* is thermotropic between "the lower temperature" and 125°. *The deeper coloured variety* is thermotropic between "the lower temperature" and the ordinary temperature, and reverts to the paler coloured variety at about 60°. Neither variety is photo-

tropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidenebromoanilines, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Br$.

Vanillylidene-m-*bromoaniline* separates from a mixture of chloroform and light petroleum in brownish-yellow crystals, which melt at 75° (corr.):

0·1852 gave 7·2 c.c. N_2 at 16° and 764 mm. N = 4·62.
$C_{14}H_{12}O_2NBr$ requires N = 4·58 per cent.

Vanillylidene-*m*-bromoaniline is dimorphous. Trituration converts it into a deep yellow, polymorphic variety, which softens at 67° and melts at 70° (corr.). Both varieties are thermotropic between the ordinary temperature and 65°. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-p-*bromoaniline* crystallises from light petroleum in pale yellow needles, which melt at 123—124° (corr.):

0·1780 gave 7·0 c.c. N_2 at 16° and 762 mm. N = 4·66.
$C_{14}H_{12}O_2NBr$ requires N = 4·58 per cent.

Vanillylidene-*p*-bromoaniline is dimorphous. On trituration, the colour changes to deep yellow. *The paler coloured variety* is thermotropic between the ordinary temperature and about 120°. *The deeper coloured variety* is not thermotropic. At 60°, the deeper coloured variety reverts to the paler coloured variety. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-p-*aminophenol*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4\cdot OH$, separates from xylene in chocolate-coloured plates, which begin to decompose at about 170°, and finally melt at 201—202° (corr.):

0·1827 gave 9·3 c.c. N_2 at 14° and 765 mm. N = 6·09.
$C_{14}H_{13}O_3N$ requires N = 5·77 per cent.

Vanillylidene-*p*-aminophenol is probably dimorphous, but the differences observed are not sufficiently marked to justify a definite statement.

Vanillylideneanisidines, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4\cdot OMe$.

Vanillylidene-m-*anisidine* separates from a solution in light petroleum in deep yellow prisms, which melt at 118—119° (corr.):

0·3339 gave 16·0 c.c. N_2 at 22° and 755 mm. N = 5·51.
$C_{15}H_{15}O_3N$ requires N = 5·45 per cent.

Vanillylidene-*m*-anisidine is dimorphous. A somewhat deeper coloured variety is produced by trituration. *The paler coloured variety* is thermotropic between "the lower temperature" and about 117°. *The deeper coloured variety* is not thermotropic, but at about 60° reverts to the paler coloured variety. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-p-*anisidine* crystallises from a mixture of chloroform and light petroleum in nearly colourless needles, which melt at 132° (corr.):

0·1768 gave 8·4 c.c. N_2 at 15° and 759 mm. N = 5·62.
$C_{15}H_{15}O_3N$ requires N = 5·45 per cent.

Vanillylidene-*p*-anisidine is dimorphous. Trituration converts it into a pale yellow variety. *The paler coloured variety* is scarcely affected by sunlight, but exhibits thermotropy between "the lower temperature" and 130°. *The deeper coloured variety* is not phototropic, but the prolonged action of sunlight converts it into a brownish-yellow *polymorphic form*. It is thermotropic between "the lower temperature," at which its colour is deeper, and the ordinary temperature. Reversion to the paler coloured variety takes place at about 80°.

Vanillylideneaminobenzoic Acids,
$OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO_2N$.

Vanillylidene-*o*-aminobenzoic acid (Pawlewski, *Ber.*, 1904, **37**, 596) crystallises from a mixture of chloroform and light petroleum in yellowish-orange needles, which melt at 169° (corr.). Pawlewski's specimen, described as amorphous, melted at 172—174°. This compound does not exhibit dimorphism when triturated, and is not affected by actinic light, but is thermotropic between "the lower temperature" and about 160°.

Vanillylidene-m-*aminobenzoic acid* separates slowly from alcohol at the ordinary temperature as a mixture of yellow and orange crystals, the whole slowly changing to orange. To these polymorphic varieties must be added a third, due to the action of solvents. The solutions in ethyl alcohol, nitrobenzene, or xylene are yellow, whilst corresponding solutions in acetone or methyl alcohol are deep red. This compound appears to be exceedingly sensitive to polymorphic change, and different specimens, apparently of equal purity, have different melting points. These are being further studied.

Vanillylidene-*p*-aminobenzoic acid.—Manchot and Furlong (*loc.*

cit.), who first prepared this compound, describe it as not crystallisable, and melting at 209°. Our specimen, crystallised with difficulty from alcohol, consists of a mixture of yellow and orange-red crystals. The orange-red variety is changed by the slightest friction to the yellow variety. The yellow needles, when recrystallised from xylene, yield yellow crystals only, which begin to decompose at about 200° and melt at 213—214° (corr.). It was noticed that an acetone solution is red, and leaves a semi-crystalline syrup on evaporation. This syrup, unlike the original compound, forms a green solution in sulphuric acid, which is changed to red by potassium hydroxide. These reactions suggest that the change is isomeric rather than polymorphic:

0·1652 gave 7·4 c.c. N_2 at 14° and 761 mm. N = 5·33.

$C_{15}H_{13}O_4N$ requires N = 5·17 per cent.

Vanillylidene-*p*-aminobenzoic acid is dimorphous. In addition to the unstable *orange-red variety* already described, the yellow needles on trituration change to *a third orange-coloured variety*. Both varieties are thermotropic between "the lower temperature" and the ordinary temperature. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidenebenzidine, $OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$. —This compound crystallises from its deep red solution in nitrobenzene in gamboge-coloured crystals. It is only sparingly soluble in other solvents. It begins to decompose at about 150°, becoming dark brown, and melts at 184—186° (corr.):

0·1488 gave 11 c.c. N_2 at 15° and 757 mm. N = 8·73.

$C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.

Vanillylidenebenzidine is dimorphous. It changes to a deep terra-cotta-coloured variety on trituration. *The paler coloured variety* is thermotropic between "the lower temperature" and the odinary temperature, and when the temperature is allowed to rise to about 170° it undergoes a permanent change in colour, and is indistinguishable from the deeper coloured variety. *The deeper coloured variety* is thermotropic between "the lower temperature" and about 170°. At the ordinary temperature the colour is deepest. It becomes paler below the ordinary temperature, and also above the ordinary temperature, till about 150° is reached; then, as the temperature rises, the colour again deepens. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light. The polymorphic form obtained from the deeper coloured variety is almost black.

Vanillylidenenaphthylamines, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_{10}H_7$.

Vanillylidene-α-naphthylamine separates from xylene in pale yellow needles, which melt at 113—114° (corr.):

0·1798 gave 8·0 c.c. N_2 at 15° and 757 mm. N = 5·25.

$C_{18}H_{15}O_2N$ requires N = 5·06 per cent.

Vanillylidene-α-naphthylamine is dimorphous. Trituration converts it into a deeper coloured yellow variety. *The paler coloured variety* is thermotropic between "the lower temperature" and 110°. *The deeper coloured variety* is thermotropic between "the lower temperature" and the ordinary temperature. It reverts to the paler coloured variety at about 60°. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent *polymorphic form* on prolonged exposure to actinic light.

Vanillylidene-β-naphthylamine separates from a mixture of chloroform and light petroleum in biscuit-coloured needles, which melt at 148—149° (corr.):

0·2002 gave 8·9 c.c. N_2 at 16° and 762 mm. N = 5·26.

$C_{18}H_{15}O_2N$ requires N = 5·06 per cent.

Vanillylidene-β-naphthylamine is dimorphous. On trituration it is converted into a yellow variety. *The paler coloured variety* is thermotropic between the ordinary temperature and about 135°. *The deeper coloured variety* is not thermotropic, but at about 90° it reverts to the paler coloured variety. Neither variety is phototropic, but both change to a deeper coloured, apparently permanent, *polymorphic form* on prolonged exposure to actinic light.

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[*Received March 8th*, 1915].

LIV.—*Organic Derivatives of Silicon. Part XXIII. Further Experiments on the So-called Siliconic Acids.*

By JOHN ARTHUR MEADS and FREDERIC STANLEY KIPPING.

THE facts recorded in our previous paper on the so-called siliconic acids (T., 1914, **105**, 689) led us to the conclusion that the silicobenzoic acid (phenylsiliconic acid) described by Ladenburg (*Annalen*, 1875, **179**, 143), and also by Khotinski and Seregenkov (*Ber.*, 1908, **41**, 2946), is not a definite compound of the molecular formula $Ph\cdot SiO_2H$, but a complex mixture of condensation

products derived from phenyltrihydroxysilicane. This conclusion was based on the results of our examination of the products obtained, under various conditions, by hydrolysing phenylsilicon trichloride with water or a dilute aqueous solution of ammonium hydroxide, and also by treating solutions of sodium phenylsiliconate with carbon dioxide or a mineral acid.

As these results and other considerations led us to believe that all the so-called siliconic acids are really mixtures of condensation products derived from the respective trihydroxides $R{\cdot}Si(OH)_3$, we proceeded to study two other typical cases. In this communication we give an account of our experiments on the preparations which have been called benzylsiliconic acid and propylsiliconic acid respectively.

It may be stated at once that the whole of our experimental evidence strongly supports the view that both these preparations are complex mixtures. The products obtained by the hydrolysis of benzylsilicon trichloride under different conditions correspond with those prepared from phenylsilicon trichloride in like manner; they all seem to consist of mixtures of compounds formed from x molecules of the trihydroxide by the elimination of x or of $x+y$ molecules of water, and, judging from the results of molecular-weight determinations, the principal components of these mixtures are condensation products derived from 3, 4, 5, and 6 molecules of the trihydroxide.

The only noteworthy difference between the preparations of the benzyl and those of the phenyl series is that the former are the more readily soluble in organic solvents, and also the more readily liquefiable. The only definite crystalline compound obtained during the study of "benzylsiliconic acid" was the sodium salt, which it may be inferred has the simple molecular formula $C_7H_7{\cdot}SiO_2Na$.

As a representative of the so-called siliconic acids of the aliphatic series we chose "propylsiliconic acid" in preference to the ethyl derivative prepared by Ladenburg and Friedel (*Ber.*, 1870, **3**, 15; *Annalen*, 1871, **159**, 259) and the methyl derivative prepared by Ladenburg (*Ber.*, 1873, **6**, 1029; *Annalen*, 1874, **173**, 143), because these two acids are described as being insoluble in all neutral liquids. This is also true of the "propylsiliconic acid" recently prepared by Melzer (*Ber.*, 1908, **41**, 3390), but by modifying the conditions of hydrolysis we hoped to be able to obtain from propylsilicon trichloride products which, being less closely related to the silicic acids than are "methylsiliconic acid" and "ethylsiliconic acid," might be soluble in neutral solvents.

The experiments which were made with this object in view were

successful; the crude product prepared from the pure trichloride under particular conditions was a mixture, about one half of which was readily soluble in cold ether, the rest being practically insoluble in all ordinary neutral solvents; the soluble portion, however, became insoluble in the course of a few days, a fact which we attribute to the occurrence of progressive condensation. The soluble product of hydrolysis, being so changeable, was not analysed, but estimations of silicon made with the insoluble product seemed to show that the latter had the composition of a "propylsiliconic anhydride." From these and other results we conclude that both the soluble and the insoluble preparations consist of mixtures of condensation products of the trihydroxide, and that the former pass into the latter either spontaneously or, more probably, under the influence of traces of alkali or acid. The very fact that we were able to foresee the probability of the existence of the soluble product of hydrolysis affords important evidence in support of these conclusions.

As in the case of the benzyl derivatives, the only crystalline substance obtained during the examination of the propyl preparations was the sodium salt, which has probably the simple molecular formula $Pr{\cdot}SiO_2Na$. These alkali salts, we believe, are so relatively easily obtained in crystals because, unlike the glue-like and other amorphous preparations of the acids, they are definite substances; in our opinion, the complex condensation products of which any given acid is composed are all hydrolysed by alkali hydroxides, forming, finally, one and the same salt.

Many attempts have been made to prepare volatile or crystalline products from the pure sodium salts of the siliconic acids, but the results have been uniformly unsuccessful. Among such experiments, attempts to prepare esters by treating the sodium salts with alkyl haloids or with methyl sulphate under various conditions may be mentioned, and also attempts to prepare the acid chlorides with the aid of phosphorus trichloride or pentachloride.

The facts regarding the so-called siliconic acids which have now been established, when considered in relation to the results of previous work which has been carried out in these laboratories, lead to important conclusions.

Silicon compounds containing the group $\vdots Si{\cdot}OH$ differ notably from their carbon analogues in very readily undergoing condensation. The monohydric silicols, $R_3Si{\cdot}OH$, although relatively stable, pass into the corresponding oxides, $R_3Si{\cdot}O{\cdot}SiR_3$, whereas the dihydric silicols, $R_2Si(OH)_2$, give various open and closed chain products, of which five different types have already been isolated (Kipping, T., 1912, **101**, 2108, 2125; Robinson and

Kipping, T., 1914, **105**, 40, 484); these different condensation products are convertible one into the other in the presence of small quantities of alkalis or mineral acids.

The obvious conclusions may therefore be drawn that the trihydric silicols, $R{\cdot}Si(OH)_3$, undergo condensation of an analogous character, and that the complex mixtures of which the so-called siliconic acids are shown to consist contain open and closed chain condensation products corresponding with those derived from the silicanediols. The final products of condensation, which are insoluble in neutral solvents and have the compositions of the anhydrides of the acids, are probably composed of closed chain compounds of great molecular complexity.

It is but a short step from these organic derivatives to orthosilicic acid, metasilicic acid, and silica, and to the corresponding compounds of tin (Smith and Kipping, T., 1913, **103**, 2034); the experimental evidence obtained during the study of the organic compounds points strongly to the conclusion that all the products derived from orthosilicic acid by the loss of the elements of water are complex mixtures of open and closed chain compounds. Since these compounds are no doubt convertible one into the other by alkalis, and probably also by mineral acids, under certain conditions they might all be very slowly transformed into one and the same end-product, crystalline silica,* but in ordinary circumstances the silica obtained from them would likewise be a complex mixture.†

The view that the aluminosilicates and allied compounds are derived from closed chain condensation products of orthosilicic acid has been put forward and discussed at some length by W. and D. Asch ("Die Silicate," 1911). These authors assume that orthosilicic acid gives rise to closed chains composed of six silicon and six oxygen atoms linked alternately, and also to similar closed chains containing five atoms of each of these elements. Starting from these assumptions, they are able to assign to many of the complex mineral silicates structural formulæ which, of course,

* If quartz is a closed chain compound produced by the condensation of many molecules of orthosilic acid, its molecule might contain asymmetric silicon groups. It is possible that the optical activity of quartz might be due to the structural asymmetry of the molecule?

† The silica which remains as a residue in the boat when an organic derivative of silicon is submitted to combustion is sometimes extraordinarily hygroscopic. In the combustion of diphenylsilicanediol, for example, the colourless residue, which was not more bulky than an equal weight of precipitated, ignited silica, rapidly increased in weight on exposure to the air and became constant when it had absorbed 16·2 per cent. of water; after having been heated several times it still showed the same behaviour.

correspond with the compositions of the respective minerals thus represented. The proof of the existence of closed chains of silicon and oxygen atoms linked alternately in the molecules of some of the condensation products of the silicanediols (Kipping, and Robison and Kipping, *loc. cit.*) lends, no doubt, some support to the views of W. and D. Asch; on the other hand, no such closed chain compound has yet been obtained which contains in its molecule more than four atoms of silicon and four atoms of oxygen.

Experimental.

Decomposition of Benzylsilicon Trichloride with Water.

As it was essential that the benzylsilicon trichloride employed in these experiments should be of a high degree of purity, the crude product was repeatedly fractionated, in the first place under diminished pressure; it was finally obtained as a colourless liquid, boiling at 215—216° under atmospheric pressure, and the yield of the pure substance was about 50 grams from 110 grams of silicon tetrachloride. The purity of the preparation was established by analysis. (Found: Cl = 46·9. $C_7H_7Cl_3Si$ requires Cl = 47·1 per cent.)

When the pure trichloride was slowly dropped into well-stirred, ice-cold water it was for the most part converted into a soluble product, and only a relatively small quantity of a glue-like solid was precipitated, but when the solution was kept during some hours, the soluble compound, possibly the trihydroxide or some simple condensation product of the latter, was slowly transformed into the insoluble glue. The solution was extracted with ether, and the extract was then treated as described in the case of the corresponding preparation obtained from phenylsilicon trichloride (Meads and Kipping, *loc. cit.*) in order to get the product in a suitable physical form. The air-dried, colourless, flaky resin thus obtained was easily powdered.

The crude "acid" melted indefinitely between 40° and 50°; it was very readily soluble in ether, benzene, chloroform, and most of the other organic solvents, but it was less readily soluble in alcohol or acetic acid, and only sparingly so in light petroleum. It was dissolved, but only very slowly, by a 25 per cent. aqueous solution of potassium hydroxide; from the concentrated alkaline solution it was immediately precipitated by hydrochloric acid, ammonium chloride, or carbon dioxide in the form of a flocculent solid, which was easily separated by filtration, and obtained as a colourless powder. Very dilute solutions of the potassium salt, however, did not give a precipitate until after the lapse of some hours, and the product in such cases was of a glue-like character.

As the crude acid could not be obtained in crystals, a sample of the air-dried preparation, obtained by hydrolysing the trichloride with ice-cold water, was submitted to a systematic course of fractional precipitation from ethereal solution with the aid of light petroleum; it was thus separated into seven fractions, each of which had been precipitated at least six times. All these fractions, when freed from solvent in a vacuum and crushed, consisted of colourless powders, which showed no sign of crystalline structure when examined under the microscope; each melted indefinitely over a range of at least 10°, and the less the solubility of the fraction the higher the temperature at which it liquefied.

The results of analyses of some of these fractions are given below; the most readily soluble fraction (I) and the most sparingly soluble fraction (VII) were not examined quantitatively:

	M. P.	C per cent.	H per cent.	Si per cent.
Fraction II.	35—45°	—	—	18·9
„ III.	35—45	55·1	5·3	19·1
„ IV.	40—50	—	—	—
„ V.	40—50	—	—	18·9
„ VI.	50—60	56·5	5·1	19·0

It will be seen that whereas the more readily soluble fraction (III) has a composition differing but little from that of a benzylsiliconic acid, the results obtained with the less readily soluble fraction (VI) correspond with those required for a mixture of the "acid" and its "anhydride," the calculated values being C=55·1 and H=5·25 for $C_7H_7 \cdot SiO_2H$, and C=58·6 and H=4·9 per cent. for $(C_7H_7 \cdot SiO)_2O$.

Molecular-weight determinations in acetic acid solution gave the following results: Fraction II, 683; Fraction III, 687; Fraction IV, 874; Fraction V, 969 and 985.

As benzylsiliconic acid would have a molecular weight of 152·4, and it does not seem very probable that such a compound would be largely associated in acetic acid solution, we conclude from the whole of the evidence that all the fractions described above are mixtures of condensation products derived from phenyltrihydroxysilicane, and that the principal components of these mixtures are compounds produced from three, four, five, and six molecules of the trihydroxide respectively.

Precipitates of Benzylsiliconic Acid obtained from Alkaline Solution.

The flocculent solids precipitated from concentrated solutions of the potassium salt of benzylsiliconic acid on the addition of hydrochloric acid or ammonium chloride, or on the saturation of the

solution with carbon dioxide, were very different from the acid obtained by hydrolysing the trichloride with water as regards their appearance; they also liquefied at rather higher temperatures than the latter, the air-dried precipitates melting gradually between 55° and 65°. Except for these rather unimportant differences, the various precipitates resembled the glue-like preparations; they were all readily soluble in most of the ordinary organic solvents except light petroleum, and separated from their solutions in the form of a viscid oil or glue, which gradually changed to a colourless, brittle solid devoid of crystalline structure. Several of these preparations were systematically fractionally precipitated from their ethereal solutions with the aid of light petroleum; the various fractions differed but little in physical properties, and they all liquefied gradually over a range of at least 10°, the most sparingly soluble portions at about 80—100°, the most soluble portions at about 50—60°; no fraction showed any sign of crystalline structure when examined under the microscope.

Decomposition of Benzylsilicon Trichloride with Steam.

When steam was passed into pure benzylsilicon trichloride, the product of hydrolysis consisted of a hard, brittle solid, which, when dried in a vacuum, melted from about 60—70°. This preparation differed notably from that obtained by hydrolysing phenylsilicon trichloride with steam (Meads and Kipping, *loc. cit.*), as it dissolved freely in ether, benzene, and other organic solvents, and was even soluble to a slight extent in light petroleum. From its solutions it separated in the form of a glue, which hardened rapidly to a brittle mass devoid of crystalline structure.

Estimations of silicon gave results (Si = 19·45 and 19·5) corresponding fairly well with those required by a benzylsiliconic anhydride (Si = 19·8 per cent.); it would seem, therefore, that in spite of the great difference in solubility between this product of hydrolysis of benzylsilicon trichloride and that obtained in a similar manner from phenylsilicon trichloride, the two are analogous in composition, and both consist essentially of a mixture of the final condensation products of the respective trihydroxy-derivatives.

Sodium Benzylsiliconate.

The sodium salt of benzylsiliconic acid was prepared by dissolving any of the preparations of the "acid" in a slight excess of an alcoholic solution of sodium methoxide; the solution was filtered from a small quantity of precipitated matter, and then left to evaporate over sulphuric acid and potassium hydroxide. The

colourless crystals of the salt, which were deposited in the course of a few days, were rapidly separated by filtration and washed with alcohol. The salt was readily and completely soluble in cold water.

Propylsilicon Trichloride.

The Grignard solution, prepared from $1\frac{1}{4}$ molecules of magnesium and an excess of propyl bromide, was cautiously added to a well-cooled and well-stirred ethereal solution of silicon tetrachloride, and the mixture was then heated on a water-bath during some hours; the product, isolated in the usual manner, boiled at 123—125°, as stated by Melzer (*Ber.*, 1908, **41**, 3390), and the yield of the pure preparation was about 30 grams from 100 grams of silicon tetrachloride. (Found: Cl = 59·0. $C_3H_7Cl_3Si$ requires Cl = 59·8 per cent.)

Decomposition of Propylsilicon Trichloride with Water.

From the results which we had already obtained during our study of the so-called siliconic acids of the aromatic series, it seemed highly probable that the insoluble preparations described by Friedel and Ladenburg (*loc. cit.*) and by Ladenburg (*loc. cit.*) as ethylsiliconic acid and methylsiliconic acid, respectively, and also the insoluble "propylsiliconic acid" recently prepared by Melzer (*loc. cit.*) by the hydrolysis of propylsilicon trichloride with ice-cold water, were really mixtures of the final condensation products of the respective trihydroxy-compounds.

On the assumption that the condensation of the initial product of hydrolysis, namely, the trihydroxide, was partly due to the local heat development which occurred during the decomposition of the trichloride, we tried to obtain a less highly condensed product of hydrolysis which we hoped would be soluble in organic solvents, and therefore more suitable for examination.

With this object in view, we passed a stream of dry air through the pure trichloride, and then led the vapour into ice-cold water, in order that hydrolysis might be accomplished without any local rise in temperature in the solution. Under these conditions, the trichloride was converted into a colourless, pasty product, about one half of which was readily soluble in cold ether, the other half being quite insoluble.

The ethereal solution gave on evaporation a colourless, glue-like mass, which dissolved freely and completely in benzene, acetone, and many other organic solvents, but was only moderately soluble in cold alcohol, and insoluble in cold light petroleum; it dissolved slowly in a 30 per cent. solution of potassium hydroxide.

From its solutions in neutral solvents, the preparation was again deposited in the form of a vitreous, readily fusible mass, in which no sign of crystalline structure could be detected under the microscope. When it had been left during some days at the ordinary temperature, either in the air or in a desiccator containing sulphuric acid, this preparation was no longer soluble in the liquids named above, and in the course of some weeks it became insoluble in all the common solvents.

An estimation of silicon made with an air-dried sample which had become quite insoluble gave Si = 30·1; the calculated percentage for a compound of the composition $Pr{\cdot}SiO_2H$ is Si = 27·2, and for a compound of the composition $(Pr{\cdot}SiO)_2O$ it is 29·8.

That portion of the product of hydrolysis of propylsilicon trichloride, which was from the first insoluble in ether, was a colourless powder, in which no trace of crystalline structure could be observed under the microscope; it was insoluble in all the ordinary solvents, as well as in neutral liquids of high boiling point, such as phenol. It dissolved only very slowly in a 30 per cent. aqueous solution of potassium hydroxide. When heated on platinum foil it did not melt, but gradually darkened in colour.

Estimations of silicon made with the dried material gave Si = 30·2 and 30·1 per cent., but it was very difficult, if not impossible, to obtain the silica free from carbonaceous matter; these results correspond fairly well with those required for a compound of the composition of propylsiliconic anhydride (Si = 29·8 per cent.).

Several combustions of these insoluble preparations were also made, and values such as the following were obtained:

I. C = 33·1; H = 6·9. II. C = 33·7; H = 7·4.

$C_3H_7{\cdot}SiO_2H$ requires C = 34·4; H = 7·3 per cent.

$(C_3H_7{\cdot}SiO)_2O$ „ C = 37·7; H = 7·3 „ „

Although the experimental results agree approximately with those required for the "acid" rather than the "anhydride," we believe that the silicon determinations are much the more trustworthy, and that the insoluble preparations have the composition of the "anhydride"; the low percentages of carbon which were actually found were certainly due, in part at least, to the great difficulty of burning the whole of the carbon, even when the substance was mixed with copper oxide or lead chromate. When burned alone in a boat in the usual manner, the substance left a residue of silica, which retained a considerable proportion of carbon even after it had been heated during many hours at as high a temperature as possible. It should perhaps be added that the analytical results given by Melzer (*loc. cit.*) for the insoluble

preparation, which he calls propylsiliconic acid, agreed, as regards carbon and hydrogen, with the calculated values, and that he did not state that he had experienced any difficulty in carrying out the combustion.

Precipitation of "Propylsiliconic" Acid from Alkaline Solution.

When the diluted, strongly alkaline solution obtained by treating "propylsiliconic acid" with a concentrated solution of potassium hydroxide was mixed with an excess of hydrochloric acid or saturated with carbon dioxide, no immediate precipitate was produced, but after some time an oily product separated. The addition of an excess of ammonium chloride to the alkaline solution caused the immediate precipitation of a similar oily product. These precipitates were quite insoluble in all the many solvents which were tried, and therefore could not be further examined.

Sodium Propylsiliconate.

Just as in the case of the phenyl and the benzyl compounds, the only crystalline derivative that we have been able to prepare from "propylsiliconic acid" is its sodium salt. This compound was obtained by treating either the insoluble or the soluble preparation described above with excess of a solution of sodium methoxide; after the lapse of some hours, the solution was filtered from a small quantity of a flocculent deposit and left to evaporate in a desiccator containing sulphuric acid and potassium hydroxide. The salt was slowly deposited in colourless needles or prisms, which were separated, and washed with alcohol; it was completely soluble in cold water.

Analyses of the salt were made by decomposing the dry sample with excess of dilute sulphuric acid, and then titrating the excess of acid; the results were Na = 17·7 and 17·6, the calculated value being 18·2 per cent.

On the addition of a slight excess of dilute acetic acid to a well-cooled solution of the sodium salt, only a relatively small proportion of the "acid" was precipitated, but when the acidified solution was then boiled, a colourless solid was thrown out of solution. When well washed and dried, this preparation was a colourless powder, but it did not melt when it was strongly heated, and it was insoluble in all the ordinary solvents.

An analysis of this product gave results (C = 34·0; H = 5·8 per cent.) which corresponded with those obtained with the other insoluble samples of "propylsiliconic acid."

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[*Received March 8th*, 1915].

LV.—*The Formation of Dialkyloxyanilines in Reduction Processes.*

By Eustace Ebenezer Turner.

While working with various di-ortho-substituted benzenes, the author had occasion to prepare 2-aminoresorcinol diethyl ether. The compound has already been described by Pukall (*Ber.*, 1887, **20**, 1136) as a very easily oxidisable substance melting at 124°. It seemed highly unlikely that Pukall's compound was actually 2-aminoresorcinol diethyl ether, since the dimethyl ether (Kauffmann, *Ber.*, 1907, **40**, 3999) is very stable and melts at 78°, and, as a rule, ethyl ethers melt at a lower temperature than the corresponding methyl ethers.

Adopting a process similar to that used by Kauffmann (*loc. cit.*) for the preparation of the methyl ether, 2-aminoresorcinol diethyl ether was obtained as a stable, colourless, crystalline substance, melting at 57°. The hydroxyazo-compound obtained by combining the diazotised amine with β-naphthol in alkaline solution and also the amine itself have been shown to have the molecular weights required by their respective formulæ.

Pukall's compound melting at 124° is therefore not 2-aminoresorcinol diethyl ether, but probably, in view of the reducing agent employed in its preparation, 4:4′-diamino-3:5:3′:5′-tetraethoxydiphenyl (see below).

This author (*loc. cit.*) showed that in the reaction between benzenediazonium chloride and resorcinol, whilst 4-benzeneazoresorcinol constituted the main product, an isomeric compound was also produced, a fact already established by Typke (*Ber.*, 1877, **10**, 1571). Corresponding with Typke's 4- and 2-benzeneazoresorcinols (m. p. 161° and 215° respectively), he isolated the corresponding ethyl ether (m. p. 70·5° and 90° respectively). Typke fractionally crystallised the crude benzeneazoresorcinols, Pukall the same mixture after ethylation.

The ether melting at 70·5° gave on reduction with alcoholic stannous chloride and hydrochloric acid the well known 4-aminoresorcinol diethyl ether (Weselsky, *Annalen*, 1872, **164**, 5; Févre, *Bull. Soc. Chim.*, 1883, [ii], **39**, 5886; Henrich and Wagner, *Ber.*, 1902, **35**, 4193).

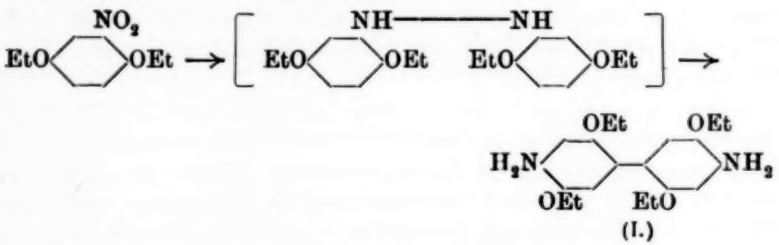
The reduction of the ortho-derivative melting at 90° would therefore be expected to produce 2-aminoresorcinol diethyl ether. Actually this is not the case.

Now the reduction of nitro- or azo-compounds with alcoholic

stannous chloride is always liable to give very abnormal results if an amine is expected. The reduction products are exceedingly varied in nature. Thus nitrobenzene is reduced to aniline by tin and aqueous hydrochloric acid, and to benzidine by alcoholic stannous chloride. More important in the present instance is the case observed by Nietzki (*Annalen*, 1882, **215**, 145), in which, by the reduction of nitroquinol diethyl ether, he obtained, not the corresponding amine, but 4:4′-diamino-2:2′:5:5′-tetraethoxydiphenyl (I), a process which the present author attributes to the intermediate formation of 2:5-diethoxyanilino-groups,

$$C_6H_3(OEt)_2\cdot NH\cdot,$$

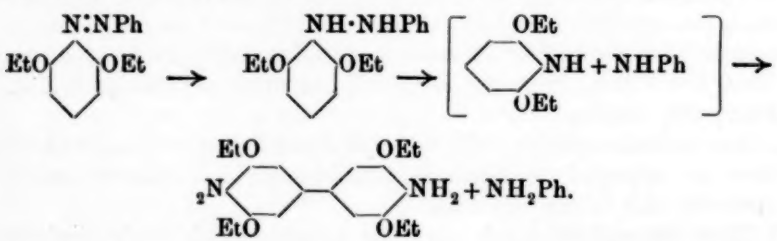
and their subsequent union (see also below).



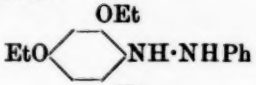
(I.)

Similarly Jacobson (*Annalen*, 1895, **287**, 97) has shown that alcoholic stannous chloride may be regarded as a specific reagent for inducing the benzidine or semidine change.

The difference in behaviour of the two isomeric benzeneazoresorcinol diethyl ethers on reduction may therefore be explained as follows: The ortho-compound gives 2:6-diethoxyhydrazobenzene, which in the presence of alcoholic stannous chloride immediately becomes highly unstable, and tends to change to a benzidine derivative. We may regard the mixture at this stage as consisting of free diethoxyanilino-groups, $C_6H_3(OEt)_2\cdot NH\cdot$, and anilino-groups. The former, in what may be called the "benzidine atmosphere," pass into the corresponding benzidine derivative (Pukall's product, m. p. 124°), whilst the anilino-groups are reduced to aniline, owing to the absence of di-ortho-substitution. This accounts for both of Pukall's products (the compound melting at 124° and aniline):



From 4-benzeneazoresorcinol diethyl ether, however, the hydrazo-compound (II) may result:



(II.)

Here, again, the production of anilino- and of 2:4-diethoxy-anilino-groups may be assumed. Since, in the latter, a substituent is present in the para-position with respect to the imino-group, the benzidine change cannot occur. Only one ortho-substituent is present, and therefore two courses are possible, namely, (1) reduction to 4-aminoresorcinol diethyl ether, or (2) ortho-wandering. Actually, the former course is preferred. At the same time the anilino-groups are reduced to aniline.

In view of Jacobson's work (*loc. cit.*), the other possible compounds were probably also present in Pukall's reduction product; he, however, only isolated the two "main products."

Experimental.

2-*Nitroresorcinol Diethyl Ether.*

This compound has been previously obtained by de Pay (*Ber.*, 1906, **39**, 2723, footnote), but details of its preparation are not given.

2-Nitroresorcinol (10 grams) is dissolved in 96 per cent. alcohol (20 c.c.) and treated with ethyl bromide (20 grams) and potassium hydroxide (7·2 grams) dissolved in water (24 c.c.). The mixture is heated in a closed vessel in a boiling-water bath for six hours. After cooling, sodium hydroxide solution is added, and the crystalline product is collected, washed with water, and recrystallised twice from alcohol.

2-Nitroresorcinol diethyl ether forms pale green or nearly colourless needles melting at 106·5° (de Pay gives 106—107°). It is soluble in the usual organic solvents, being best crystallised from alcohol. (Found, C=57·1; H=6·3; OEt=42·6. Calc., C=56·9; H=6·2; OEt=42·7 per cent.)

2-*Aminoresorcinol Diethyl Ether.*

2-Nitroresorcinol diethyl ether is warmed with the calculated amount of granulated tin and concentrated hydrochloric acid on the water-bath until solution is complete. The product is treated with an excess of sodium hydroxide solution and repeatedly extracted with ether. The united extracts are dried and evaporated, and the product is recrystallised from petroleum (b. p. 30—50°):

0·1056 gave 0·2579 CO_2 and 0·0803 H_2O. C = 66·6; H = 8·5.
0·1194 „ 8·14 c.c. N_2 (moist) at 19° and 754 mm. N = 7·8.
Found, M.W.(by cryoscopic method in benzene) = 175, 191.

$C_{10}H_{15}O_2N$ requires C = 66·3; H = 8·3; N = 7·7 per cent.
M.W. = 181.

2-Aminoresorcinol diethyl ether forms colourless needles melting at 57° (uncorr.). The ethereal solution is very stable, and both this and the solid base can be kept in the open air for weeks without change of colour or of melting point.

By employing glacial acetic acid instead of hydrochloric acid in the reduction, the process is very much slower, but a somewhat purer product is obtained.

The colourless *hydrochloride* is obtained by passing dry hydrogen chloride into a solution of the base in benzene or light petroleum.

The *platinichloride*, prepared in the usual manner, is a very well-defined salt forming reddish-yellow needles (small crystals are very nearly colourless):

0·3838 gave 0·0959 Pt. Pt = 25·0.
$(C_{10}H_{15}O_2N)_2,H_2PtCl_6$ requires Pt = 25·25 per cent.

The molecular weight of the free amine was confirmed by determining that also of the following hydroxyazo-compound.

2:6-Diethoxybenzeneazo-β-naphthol is obtained by adding the diazotised amine to β-naphthol in alkaline solution. It separates from solutions in glacial acetic acid in deep red plates with a bright green reflex. The substance melts at 104° when heated slowly, but the melting point varies with the rate of heating:

0·1097 gave 7·8 c.c. N_2 (moist) at 21° and 768 mm. N = 8·2.
Found, M.W.(by cryoscopic method in benzene) = 310, 314, 324.
$C_{20}H_{20}O_3N_2$ requires N = 8·3 per cent. M.W. = 336.

Reduction of 2-Nitroresorcinol Dimethyl Ether.

Kauffmann, after reducing 2-nitroresorcinol dimethyl ether with tin and hydrochloric acid, adding an excess of sodium hydroxide, extracting with ether, and recrystallising the ethereal residue from alcohol, obtained a substance which he regarded as consisting solely of 2-aminoresorcinol dimethyl ether; in order to effect further purification he recrystallised the substance from alcohol. On working in this way the mother liquors have always been found to contain a second compound (separated from the first by conversion into the platinichlorides and fractionally recrystallising) in varying amount (in one case 30 per cent. of the product, but usually not

more than 10 per cent.) and containing chlorine. Whilst the purification of Kauffmann's dimethyl ether presented no difficulty (although alcohol is less efficient than light petroleum as a solvent), the chloro-compound was with difficulty obtained in a pure state, owing to the persistent way in which the two amines formed mixed crystals. Fractional crystallisation from light petroleum of the residue obtained after evaporating the mother liquors yielded products which, although splendidly crystalline, proved to be mixed crystals of the two amines. Thus three analyses of a solid melting at 36° (obtained persistently) gave the following figures: (*a*) C=54·8; H=5·94; (*b*) C=54·7; H=6·02. (*c*) C=54·9; H=5·94. Evidently the stability of the solid solutions is considerable, and would probably repay investigation from a physical point of view.

Finally it was found possible by distillation under diminished pressure to effect the desired separation. The ethereal extracts from the reduction process were evaporated, and the residue was distilled under 15 mm. pressure, when the pure dimethyl ether boiled at 140°. As soon as the temperature began to rise above this point, the distillation was discontinued. The residue was practically pure chloro-2-aminoresorcinol dimethyl ether.

2-Aminoresorcinol dimethyl ether crystallises from light petroleum in large, perfect, tetragonal prisms, exhibiting a bluish-pink tinge. (Found, C=62·7; H=7·3; OMe=39·6, 39·4. Calc., C=62·7; H=7·2; OMe=40·5 per cent.)

The *hydrochloride* is obtained either by passing hydrogen chloride through a solution of the base in benzene or light petroleum, and recrystallising the product from alcoholic hydrochloric acid, or by warming the base in a slow current of hydrogen chloride, and re-subliming the hydrochloride in a stream of the same gas.

In both cases the salt is obtained in long, colourless needles:

(By method I) 0·2656 gave 0·2030 AgCl. Cl=18·9.
(By method II) 0·1730 „ 0·1324 AgCl. Cl=18·9.
$C_8H_{11}O_2N,HCl$ requires Cl=18·73 per cent.

The *platinichloride* forms almost colourless needles, which become orange-yellow on exposure to light:

0·1190 gave 0·0323 Pt. Pt=27·1.
$(C_8H_{11}O_2N)_2,H_2PtCl_6$ requires Pt=27·2 per cent.

Chloro-2-aminoresorcinol Dimethyl Ether.

The residue from the distillation process described above was recrystallised from light petroleum, when the base separated in tufts of slender, colourless needles, melting at 50° (uncorr.):

0·1416 gave 0·2669 CO_2 and 0·0684 H_2O. C = 51·4; H = 5·4.

0·1058 „ 0·0794 AgCl. Cl = 18·6.

$C_8H_{10}O_2NCl$ requires C = 51·2; H = 5·3; Cl = 18·9 per cent.

The *hydrochloride* is a well-defined, colourless salt. Its diazotised solution combines with β-naphthol in alkaline solution to form a hydroxyazo-compound somewhat darker than the non-chlorinated compound.

The *platinichloride* crystallises in rosettes of needles, and has a deeper colour than that of 2-aminoresorcinol dimethyl ether:

0·3490 gave 0·0872 Pt. Pt = 25·0.

$(C_8H_{10}O_2NCl)_2,H_2PtCl_6$ requires Pt = 24·8 per cent.

Replacement of the Amino- by the Hydroxyl Group.

An attempt was made to convert 2-aminoresorcinol dimethyl ether into pyrogallol dimethyl ether by using the method recommended by Cain (T., 1906, **89**, 19), since the method used by Kauffmann was unsuccessful. The diazotised solution was treated with a large quantity of sulphuric acid (1:1) and potassium sulphate, and distilled in a current of superheated steam. The temperature rose to 160°, and a gas, presumably nitrogen, was rapidly evolved. A clear distillate was obtained, from which a small amount of a substance, having the properties of pyrogallol dimethyl ether, was extracted by ether. The substance could not be obtained pure, but on treatment with chromic and glacial acetic acids the solution rapidly deposited long, glistening needles of cœrulignone. This dissolved in concentrated sulphuric acid to give the well-known, characteristic cornflower-blue coloration.

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[*Received February 13th*, 1915.]

LVI.—*Velocity of Crystallisation from Aqueous Solutions.*

By Norman Phillips Campbell.

Investigations on the velocity of crystallisation have been concerned chiefly with the influence of the conditions of the liquid phase, such as the degree of supersaturation or superfusion and the presence of foreign substances. It seemed desirable to develop a method that would eliminate these influences, in order to isolate the factors which are concerned with the surface receiving the crystalline deposit. Where the surface has been taken into account by previous experimenters, it has been assumed that the velocity of crystallisation is proportional to the area of the surface exposed to the liquid.

The method employed was to hang in a slightly supersaturated solution of potassium alum two weighed alum crystals as nearly perfect as possible. The solution being stirred and the temperature slowly falling, the crystals grew very regularly and rapidly. At the end of about fourteen hours the crystals were taken out, dried, and weighed. From the increase in weight the relative thickness of the layer of substance deposited could be calculated. The same crystals were subjected to a series of such periods of growth. The advantage of the method is its simplicity and the rapidity with which determinations may be made.

The results of the experiments were as follows:

(*a*) The method justified itself, giving concordant results in any one series of observations. For example, from the weight of the one crystal that of the other could be predicted from the formula to an accuracy of about 1 per cent. Since in most of the series of experiments the crystals doubled in weight several times, an accuracy of 1 per cent. is quite sufficient to establish a law of crystal growth. Further, the relative areas of the surfaces of two crystals, calculated from their weights, agreed to an accuracy of about 1 per cent. with that obtained by direct measurement with a reading microscope, thus affording an independent check upon the method of weighing.

(*b*) The method may be used to establish accurately the customary assumption that the rate of growth on similar crystal faces is proportional to the area of the faces exposed to the liquid. This means that large crystals and small crystals receive deposits of equal thickness in the same time. This result is not in accordance with the general belief that a large crystal grows at the

expense of small ones, unless, through the solution becoming unsaturated, the small crystals dissolve altogether. Also the result does not agree with the conclusion drawn by Richards and Archibald (*Amer. Chem. J.*, 1901, **26**, 61) from instantaneous photographs of very small crystals growing in highly supersaturated solutions. These authors found $m = kt$ (m = mass of crystal, t = time), whereas, according to the results obtained in the experiments described here, $m^{\frac{1}{3}} = kt$.

(*c*) In some experiments in which the solution contained a certain impurity, potassium alum crystals were obtained as almost perfect cubes having not even the smallest octohedral faces.

Experimental Details and Calculation of Results.

The Solution.—No special precautions were taken to purify the alum, as it did not seem probable that small amounts of impurities would have much influence on the relative rate of growth. A small quantity of sulphuric acid was added, as it was found that alkaline impurities favour the development of cube faces. During the day, the solution was kept in contact with coarsely powdered alum, or allowed to drop through a filter funnel packed with alum crystals, the temperature being about 25°. About 5 p.m. the solution, free from small crystals, was poured into a vessel containing the weighed crystals, the temperature being about 23°. Thus a convenient degree of supersaturation was maintained, mainly by means of a slight fall of temperature, and very slightly by means of evaporation. It was found that the solution was still slightly supersaturated next morning, when the crystals were taken out and weighed. Owing to the small difference between the day and night temperatures at Kandy, it was easy, without a thermostat, to keep the variation of temperature within convenient limits, not more than 4°, provided that a fairly large quantity of solution was used.

The crystals were started from small nuclei on hairs. Their weights ranged from 0·1 to 30 grams. Only with the largest crystals was difficulty experienced, owing to the breaking of the support. The octahedral faces in a given crystal were seldom quite equally developed, and there were usually small cube faces, amounting to about 1 per cent. of the total surface. These irregularities do not affect the calculations, the ratio of the surface area to the volume of the crystals not being appreciably different from that for perfect octahedra. The faces were usually beautifully plane, and vicinal faces were often observed. No difficulty was experienced in drying a crystal with filter paper, so that its weight did not afterwards alter by 0·1 mg.

The crystallisation apparatus consisted of a cylindrical vessel having a capacity of about 1½ litres, and provided with a central stirrer, usually of the inverted T-shape. Care was taken to suspend the crystals from rigid supports so that their centres should be at equal distances below the surface and at equal distances from the axis of the stirrer. It was hoped that by this means the crystals would be subjected to a stream of solution flowing at the same rate for both. It was found, however, that a slight alteration in the position of the crystals considerably affected their relative rates of growth, presumably because one received a faster stream than the other. Various forms of stirrers were tried without success. One series, in which the solution was placed in a desiccator and not stirred at all, gave no better results. It is hoped that the desired uniformity may be obtained in future experiments by moving the crystals backwards and forwards side by side in parallel lines.

The Calculation.—If a crystal grows without change in shape, and if the rate of growth is proportional to the area of the surface, then

$$dm/dt = km^{\frac{2}{3}},$$

where m = mass of crystal,

t = time,

k = constant depending on the degree of supersaturation, the rate of flow of the solution, and perhaps other factors.

It is assumed that k is the same for two crystals of the same form symmetrically placed in the same solution, for example, for the two alum crystals used in these experiments. Hence, if m_1 and M_1 are the masses of the crystals at a given instant, and m_2 and M_2 the masses at some later instant, then

$$(m_2^{\frac{1}{3}} - m_1^{\frac{1}{3}})/(M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}}) = 1.$$

In all the experiments this ratio remained almost constant so long as the conditions, such as stirring and the position of the crystals, remained constant, but it was rarely equal to unity; it varied between 0·85 and 1·18 for different series of experiments. Using the same pair of crystals, a change in the form of the stirrer always produced a sudden change in the constant. This clearly points to the conclusion that the above law would be followed accurately if an arrangement could be devised for growing the two crystals under identical conditions. Assigning to the factor a value found by interpolation, the agreement between the observed and the calculated values is as close as could be expected, as is seen from the following results:

	Observed. M. grams.	Observed. m. grams.	m. Calculated from formula.	Percentage difference between m observed and calculated.	$\frac{m_2^{\frac{1}{3}} - m_1^{\frac{1}{3}}}{M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}}}$	
Series A.	3·3799	0·2281	0·2373	+3·9	1·16	
	4·1648	0·4001	0·3986	−0·4	1·04	
	4·8310	0·5544	0·5596	+0·9	1·11	1·08
	5·7218	0·8051	0·8040	−0·1	1·07	
	6·8805	1·1620	1·1648	+0·2	1·09	
	8·0690	1·5794	1·5794	0·0	—	
Series B.	8·069	1·579	1·552	−1·8	0·83	
	11·595	2·622	2·653	+1·2	0·88	
	14·100	3·462	3·501	+1·1	0·94	
	16·865	4·516	4·484	−0·7	0·82	0·88
	19·119	5·296	5·322	+0·5	0·92	
	22·541	6·671	6·633	−0·5	—	
Series C.	0·7214	0·1045	0·1037	−0·8	1·05	
	0·8540	0·1451	0·1471	+1·4	1·18	
	0·9080	0·1652	0·1660	+0·5	1·17	
	0·9619	0·1860	0·1862	+0·1	1·13	
	1·1792	0·2739 / 0·2732 *	0·2731 / 0·2724	−0·3	1·17	1·12
	1·3970	0·3743	0·3684	−1·6	1·07	
	1·7273	0·5287	0·5283	−0·1	1·11	
	2·1300	0·7402	0·7429	+0·4	—	
Series D.	0·3836	0·1810	0·1815	+0·2	1·11	
	0·4743	0·2442	0·2447	+0·2	1·25	
	0·5219	0·2830	0·2788	−1·5	1·10	
	0·6119	0·3500	0·3460	−1·2	1·17	
	0·7214	0·4400	0·4305	−2·0	0·98	1·11
	0·8540	0·5344	0·5366	+0·4	1·16	
	0·9080	0·5808	0·5808	0·0	1·08	
	0·9619	0·6242	0·6255	+0·2	1·12	
	1·1792	0·8099	0·8102	+0·04	—	
Series E.	2·1303	0·7415	0·7436	+0·3	1·21	
	2·7852	1·1609	1·1430	−1·6	1·08	
	3·1859	1·4056	1·4056	0·0	1·18	
	3·5792	1·6800	1·6756	−0·3	1·18	1·16
	4·1345	2·0853	2·0737	−0·5	1·12	
	4·9250	2·6617	2·6671	+0·2	1·17	
	5·2710	2·9348	2·9379	+0·1	—	

* A small piece was accidentally broken from the crystal during weighing.

In the first two columns are given the weights of the crystals. Numbers opposite one another are the weights at the same instant of two crystals suspended in the same solution. The numbers in the vertical column of any series are the successive weights of a single crystal at intervals during its growth. The interval between two consecutive weighings is about fourteen hours in series A, B, and E, and about twenty-four hours in series C and D. The times are not recorded, as it is not the absolute rate of growth of one crystal, but the relative rate of growth of two, that is considered.

In series A and B the solution was stirred as described above. The two really form one series, as the same pair of crystals was used for both, but in B the stirrer revolved faster than in A, and was somewhat differently adjusted. It will be seen that this alteration in the stirrer produced an immediate and marked alteration in the constant, changing it from 1·08 to 0·88. Doubtless in A the solution flowed past the crystal *m* somewhat more rapidly than past the crystal *M*, whereas in B the reverse was the case. In series C and D the solution was still, and kept in a desiccator. C and D run part of their course concurrently, that is, three crystals were hung in the solution, the calculation being made by taking them in pairs. In series E the crystals themselves were rotated about a vertical axis. All the crystals were weighed to 0·1 mg., but in series B the crystals were so large and the growth so rapid that the fourth place of decimals has no significance. It will be seen that the weight of one crystal, calculated from that of the other by the formula, agrees with the observed values within 2 per cent. in all cases except one, and in most cases it agrees within 1 per cent. About thirty other weighings were taken with other pairs of crystals with a view to finding a suitable method of stirring, but the results are not recorded here, as they add nothing new to the above.

Direct Measurement of the Area of the Surface of the Crystals.—The area of the faces was determined from the length of their edges, measured to 0·01 mm. with a travelling microscope. The following is an example of the measurement:

	Crystal A.	Crystal B.
Area of octahedral faces	637·66 sq. mm.	309·54 sq. mm.
Area of cubic faces	2·58 sq. mm.	3·11 sq. mm.
Total Area	640·24 sq. mm.	312·65 sq. mm.
Weight	2·1300 grams	0·7402 gram

$$\text{Area of A}/\text{Area of B} = 2{\cdot}048.$$
$$(\text{Weight of A}/\text{Weight of B})^{\frac{2}{3}} = 2{\cdot}023.$$

Neither of these crystals was quite "perfect," because their octahedral faces were not all equally developed, the largest octahedral face on crystal B having an area of about 47 sq. mm., the smallest only 30 sq. mm. Yet the agreement between the two entirely independent methods of calculating the relative areas shows that, even with crystals so far from perfect octahedra as these were, the surface areas are proportional to the two-third power of the masses to an accuracy of about 1 per cent. As the measurements and calculations were very tedious, they were made for a few pairs of crystals only, merely as a check on the method of weighing. The following are the results with two large crystals

of nearly the same size, but again with faces rather unequally developed:

Ratio of areas in sq. mm. = 8717·7/8665·6 = 1·006.
(Ratio of weights)$^{\frac{2}{3}}$ = (30·5885/30·4650)$^{\frac{2}{3}}$ = 1·003.

Cube Crystals of Alum.—With a view to comparing the rate of growth of the cubic and the octahedral faces of alum, some experiments were made on the conditions which favour the development of cubic faces. As is well known, sodium carbonate or carbamide, when added to the alum solution, causes cubic faces to appear, but the crystals thus obtained are always a combination of the octahedron and the cube. It was found, however, that Portland cement added to potassium alum solution caused the complete suppression of the octahedral faces. The crystals grew as easily as ordinary alum crystals, and could be obtained in a few days in quite large "perfect" cubes. When the cubes were recrystallised from water they assumed the ordinary octahedral form. It is not known whether the change in habit of alum can be induced by one of the constituents of Portland cement alone.

Two Solid Phases.—In a solution saturated with regard to both potassium alum and potassium dichromate, an alum crystal and a potassium dichromate crystal, hung side by side, will both grow with quite perfect faces. Interesting results may possibly be obtained by comparing the rate of growth of the two crystals under these conditions, but as the experiments have to be postponed indefinitely, it was thought best to publish the results obtained with alum alone.

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[*Received March 8th*, 1915.]

LVII.—*The Reaction Between Calcium Hydroxide and Sulphur in Aqueous Solution.*

By SAMUEL JAMES MANSON AULD.

OWING to the present circumstances the immediate continuation of this work is impossible, and the results obtained are therefore placed on record, although they are less complete in some particulars than is desirable.

The lime–sulphur wash, which is used extensively as a fungicide, is prepared by boiling together one part of quicklime, two or more parts of sulphur, and ten parts of water. The concentrated com-

mercial product generally contains the polysulphides, thiosulphate, sulphite, and sulphate of calcium; the polysulphides and the thiosulphate preponderate. It is usually stated that the polysulphides present are CaS_4 and CaS_5, and van Slyke, Hedges, and Bosworth (*N.Y. Agric. Expt. Stat.*, 1910, 329, 433) claim to have obtained these compounds as crystals from the concentrated lime–sulphur wash. When exposed to the air the solution gradually becomes colourless, and deposits sulphur and calcium sulphite, and the content of calcium thiosulphate increases. For this reason the course of the original reaction cannot be followed by examining the solution prepared by boiling, or which has been stored, in contact with air.

Of the polysulphides of calcium which may exist in solution little is known. The disulphide, CaS_2, is stated to exist (Roscoe and Schorlemner, 5th edition, Vol. II., 551, and other English textbooks), but the author can find no reference to this compound in the literature, nor is it mentioned in the modern handbooks of Gmelin-Kraut, Abegg, Moissan, or Dammer. The existence of the tetrasulphide, CaS_4, also, is apparently only assumed from the original work of Schöne (*Jahresbericht*, 1861, 122), who states that the compound $4CaO,CaS_4,18H_2O$ is formed when sulphur is boiled with calcium monosulphide in insufficient quantity to produce CaS_4. The latter has not itself been separated, and according to Divers and Shimidzu (T., 1884, **45**, 282) does not exist, calcium pentasulphide only being formed when sulphur is dissolved in a solution of calcium hydrosulphide. The pentasulphide has been well characterised by the latter investigators. Disregarding the statements of van Slyke (*loc. cit.*), which cannot be confirmed, it may be taken that the only polysulphide of calcium at all definitely known is CaS_5. Assumptions of the existence of CaS_4 in solution when the ratio of Ca : S lies between 1 : 4 and 1 : 5 are not well founded, and the ratios may equally well be explained by the presence of other polysulphides, and particularly of those lower than CaS_4, since the bulk of the evidence points to the existence in solution of the pentasulphide.

There is no doubt that much of the sulphur in the lime–sulphur solution is in a very loosely combined condition, and Tartar and Bradley (*J. Ind. Eng. Chem.*, 1910, **5**, 271) have already attempted to characterise the polysulphides by extraction with sulphur solvents. They obtained indications of the existence of a lower, stable calcium polysulphide which may have been the disulphide. The preliminary experiments of the present investigation, carried out five years ago, had already tended to show the looseness of combination of much of the sulphur is the higher polysulphides of

calcium present in the lime–sulphur wash, but objection arose to these and to the results of Tartar and Bradley on account of the non-exclusion of oxygen and carbon dioxide, both during the preparation of the wash and its subsequent examination. In order to eliminate the complications due to the secondary liberation of free sulphur, the reaction has now been carried out in an atmosphere of inert gas in an apparatus so devised that the resultant liquid can be collected and examined without coming in contact with oxygen or carbon dioxide.

Extraction of the fluid with sulphur solvents causes a continuous removal of free sulphur. Tartar and Bradley (*loc. cit.*) assumed that the continuous removal of sulphur was caused by oxidation of the polysulphides, but the most rigorous exclusion of air during the exhaustion of the lime–sulphur fluid does not give any more definite end-point. The continuous formation of sulphur is due, rather, to the hydrolytic dissociation of the polysulphides, which accounts also for the strongly alkaline nature of the wash. Since, also, hydrogen sulphide is readily liberated in quantity when the liquid is heated, the formation of the sulphur is likely to be due to the following equilibria:

$$CaS_x + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2S_x$$
$$H_2S_x \rightleftharpoons H_2S + (x-1)S.$$

Attempts have been made to detect the existence of a more stable polysulphide in solution by measuring the sulphur removed from the wash at stated intervals, and although, by themselves, the results cannot be regarded as conclusive owing to the experimental difficulties, yet it is significant that a lower rate of extraction sets in when the ratio between the polysulphide sulphur (S_P) plus monosulphide sulphur (S_M) and the monosulphide sulphur alone is between 1·6 and 2·3.

Extraction experiments were also repeated on the dry residue obtained by evaporating the liquor in a manner somewhat similar to that adopted by Tartar and Bradley, but the dried wash was kept under the surface of the extracting liquid during the whole time. By passing purified nitrogen through the apparatus any possible secondary decomposition was avoided. The residual material, from which sulphur is only very slowly removed, represents a more stable polysulphide than those composing the main bulk of the lime–sulphur solution. It was impossible, however, to ascribe any definite formula to the residue, the composition of which varied each time the extraction was carried out. The ratio

$$(S_P + S_M)/S_M$$

was generally less than 2, although in one instance it approached this figure. From these experiments alone it is impossible to

suggest a definite formula for the lower stable polysulphide of calcium, but it is significant that the "whole-number" polysulphide nearest in composition is CaS_2.

Attempts were made to prepare calcium disulphide by boiling together lime and sulphur in the calculated proportions (compare Roscoe and Schorlemmer, *loc. cit.*), but in every case Herschell's crystals were obtained. The composition of Herschell's crystals was first seriously examined by Schöne (*loc. cit.*), who assigned them the formula $3CaO,CaS_4,12H_2O$, but this work was later traversed by Geuther (*Annalen*, 1884, **224**, 178), who recorded the formula $2CaO,CaS_3,10H_2O$. Elementary analysis shows very little difference between the empirical formulæ as given by Schöne and by Geuther and the formula $CaO,CaS_2,7H_2O$, except in the content of water of crystallisation. This figure is the most difficult to determine. Preparations of the crystalline substance were analysed, and the ratio of polysulphide- to monosulphide-sulphur determined. The results show that the main product corresponds with the formula $CaO,CaS_2,7H_2O$, but indications were obtained of the existence of similar, probably isomorphous substances of different composition.

The existence of the complex CaS_2 throws light on the formation and the constitution of the higher calcium polysulphides, for in the circumstances it is justifiable to draw the conclusion that the CaS_2 complex, probably in attachment to CaO, is first formed whenever sulphur and lime are boiled together, and that the subsequently formed higher polysulphides still contain the complex. In this connexion it is noteworthy that Schenk and Falcke (*Ber.*, 1908, **41**, 2600) indicate hydrogen disulphide, H_2S_2, to be the most stable hydrogen polysulphide, especially in the presence of alkali.

Tartar (*J. Amer. Chem. Soc.*, 1914, **36**, 495) is of opinion that the first-formed polysulphide is the tetrasulphide, CaS_4, his reasons being (1) when an excess of sulphur is boiled with lime the ratio of polysulphide to monosulphide lies between 4 and 5, this being reduced to 4 by treatment with an excess of lime; (2) when the proportions of sulphur and lime are those calculated for CaS_4, the ratio becomes actually 4. The latter, the more cogent, contention is incorrect, as will be seen later (compare also van Slyke, Bosworth, and Hedges, *loc. cit.*, 1910, p. 417), but if it is correct it does not preclude the initial formation of calcium disulphide, and the subsequent building up of either $CaS_2,xCaO$ or CaS_2,yS, according as lime or sulphur is in excess. Tartar's conclusion is the more surprising in view of Tartar and Bradley's work, quoted above, on the probable existence of a stable lower polysulphide.

It appears, therefore, that the course of the reaction between calcium hydroxide and sulphur in aqueous solution is probably primarily:

$$5Ca(OH)_2 + 6S = 2(CaS_2,CaO) + CaS_2O_3 + 5H_2O,$$

the other polysulphides being formed with an excess of sulphur as follows:

$$CaS_2,CaO + xS + H_2O = CaS_{x+2} + Ca(OH)_2.$$

Constitution of the Polysulphides.

The constitution of the polysulphides has been frequently discussed. Apart from their popular formulation as $R_2{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}\cdot$ (compare Blanksma, *Rec. trav. chim.*, 1900, **20**, 146), the most important suggestions have been made by Geuther (*loc. cit.*) and by Küster and Heberlein (*Zeitsch. anorg. Chem.*, 1905, **43**, 53). Geuther's formula is cumbersome, and depends on the variable valency of the metallic radicle. For the polysulphides of sodium Küster and Heberlein offer a constitution which regards them as salts of the complex thio-acids, thus: $H_2S{\cdot}S$, $H_2S{\cdot}S_2$, $H_2S{\cdot}S_3$, etc.

From the present work it appears that the calcium polysulphides may be best formulated as CaS_2,S_x, or, more fully, as:

$$Ca\left<\begin{matrix}S\\ \|\\ S\end{matrix}\right>S{:}S{:}S{:}\ \ldots$$

On the simplest assumptions possible this allows the existence of all the "whole-number" calcium polysulphides from the disulphide upwards. Many of these possibly do exist in the solution obtained by boiling lime with excess of sulphur and water, there being great difficulty, however, in their actual isolation or even their detection. The constitution suggested agrees with observed facts, as, for example, that all polysulphides with ethyl bromide or ethyl iodide give only ethyl disulphide, and explains the looseness of attachment of most of the polysulphide sulphur. It implies that as the chain lengthens the sulphur atoms or complexes last added are so loosely combined as to behave practically as sulphur in solution. The question arises, however, as to the possible length of the chain, and whether, as is generally assumed, the pentasulphide is the highest existent. It has already been pointed out that, in the boiling liquid, prepared in the absence of air, more sulphur is dissolved than remains in solution on cooling. In the hot liquid the ratio $(S_P+S_M)/S_M$ frequently exceeds 5, implying the existence, at least, of the hexasulphide, CaS_6. The addition of mineral acids, also, does not cause a permanent precipitation of sulphur from the polysulphide liquor until an appreciable quantity of acid has been added. This effect is not due to the formation

of hydrogen polysulphides, but to the re-dissolving or retaining in solution of the sulphur primarily set free. At the highest temperatures the polysulphidic sulphur retained in solution may have raised the S_P:S_M ratio so high (the monosulphide being correspondingly reduced) as to correspond with the existence of CaS_8 or CaS_9. Although such high polysulphides may not necessarily be present to any extent in the normal lime–sulphur liquid, yet their possible existence and behaviour offers an explanation of the varying composition and of the properties of the liquid, and would imply the presence of a mixture, probably in equilibrium, of a wider range of polysulphides than has hitherto been assumed.

Experimental.

The materials used in these experiments were of a high standard of purity. The sulphur employed was the pure large crystals of commerce, recrystallised from carbon disulphide, and ground to a fine powder. The quicklime was calcium oxide prepared from marble; it was stored in a dry atmosphere free from carbon dioxide.

Apparatus.

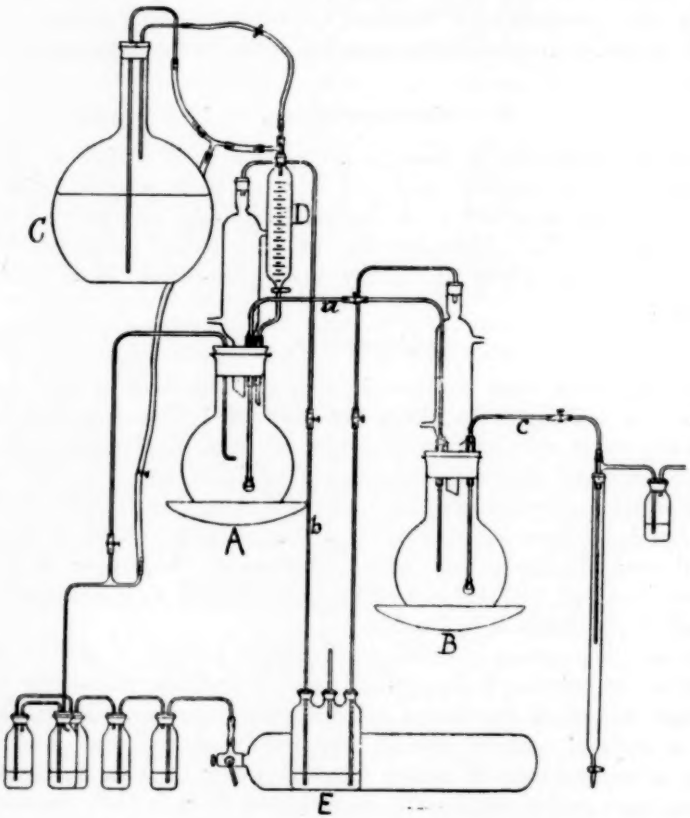
The apparatus used is shown in Fig. 1. The flasks *A* and *B*, in which the boiling takes place, are each of 1 litre capacity, and specially made with extra-wide necks, 63 mm. in diameter. Flask *A* is connected (1) with the supply of inert gas, (2) with the flask *B*, and (3) through the graduated dropping funnel *D* with the supply of lime-water or milk of lime. Both boiling flasks are fitted with double-surface reflux condensers, the upper ends of which are fitted with tubes leading to the bottle *E*, which contains bromine and sodium hydroxide.

In carrying out an experiment the major portion of the weighed quantity of sulphur is introduced into *A* and the remainder into *B*, and the whole apparatus fitted tightly together. Previous to this a stock of milk of lime is prepared by slaking the quicklime in a known amount of boiled distilled water in flask *C*, through which inert gas is continually passed; the flask is then connected as explained. The inert gas is now passed through the whole apparatus until all oxygen and carbon dioxide are expelled, each successive section being cleared out separately by manipulating the various screw clips. The gas originally used was hydrogen, but this suffers from many disadvantages, and it was replaced by nitrogen, which was purified by bubbling through sulphuric acid, strong aqueous sodium hydroxide, and pyrogallic acid and sodium hydroxide. When all air has been displaced from the apparatus,

the flask *C* is well shaken, and the calcium hydroxide run into *D*, and from thence to the boiling flask.

The sulphur and lime are boiled together for the desired time (generally one and a-half hours), during which the tube *a* is closed and *b* open. The siphon-tube *a* is now lowered through the seal. The seal is constructed of a close-fitting, short glass tube surmounted by "pressure" rubber-tubing; when slightly lubricated

FIG. 1.



with petroleum jelly this gives very tight-fitting yet adjustable junctures. By continuing to boil the liquid in *A*, the siphon is set and the liquid passes over into *B* after having been filtered through a small plug of cotton-wool surrounded by glass-wool and held in position with muslin.

The boiling process is similarly repeated in *B* with the remainder of the sulphur, possible contamination with free lime from *A*

being thus avoided. Eventually the filtered liquid is drawn off through the siphon *c*, either into the large burette for analysis or into vessels contained in a desiccator for evaporation or other examination.

By the use of this apparatus it is possible to examine the liquid thoroughly without its coming into even passing contact with the atmosphere. If necessary, the amount of hydrogen sulphide liberated during boiling can be measured by an examination of the oxidising liquid in *E*.

Calcium Hydroxide and Excess of Sulphur.

The following typical experiments were carried out as described above, using a 30 per cent. milk of lime. The resulting liquids were drawn off either while boiling or after allowing to cool in *B* to room temperature. In each experiment the proportion of sulphur to lime was not less than 100 to 30. The percentages shown are grams per 100 c.c. of liquid.

TABLE I.

			Sulphur in solution.						
Expt. No.	Temp. of drawing off.	Sulphur deposited per cent.	Total per cent.	Monosulphide per cent.	Polysulphide per cent.	Thiosulphate per cent.	Total CaO per cent.	Ratio $(S_M+S_T)/S_M$.	Ratio S/CaO.
1	b.p.	0·194	7·40	1·01	3·54	2·85	3·30	4·50	2·24
2	18°	—	1·61	0·26	0·86	0·43	0·68	4·30	2·36
3	18°	—	1·89	0·32	1·06	0·51	0·69	4·31	2·70
*4	18°	—	8·08	1·24	5·08	2·08	—	5·10	—
5	b.p.	appreciable	13·17	2·08	8·13	3·06	6·02	4·90	2·20

* This solution deposited sulphur after a few hours.

The analyses do not allow of the existence of sulphur compounds other than calcium polysulphides and calcium thiosulphate, nor is there any free lime present. This is confirmed by qualitative examination. The absence of calcium hydrosulphide is proved by the fact that no hydrogen sulphide is formed on the addition of manganous sulphate.* The composition of the liquid is largely a

* It is true that Ramsay (*J. Agric. Sci.*, 1914, **6**, 194), assuming that the "monosulphide sulphur" should be present as actual CaS, explains certain properties of the liquid by the existence of the equilibrium $CaH_2S_2 + CaH_2O_2 \rightleftharpoons 2Ca(HS)(OH)$. The hydroxyhydrosulphide, however, is immediately decomposed by water with the formation of the hydrosulphide, which alone is stable in solution (Divers and Schimidzu, *loc. cit.*) and therefore determines the reaction with manganous sulphate.

function of the time of boiling, since the thiosulphate tends to increase with the continued removal of hydrogen sulphide, and consequently reduces the S/CaO ratio. Since this ratio is thus entirely dependent on the hydrolysis of the polysulphides during the boiling process, it affords no indication either of the course of the reaction or the fungicidal value of the liquid.

The second boiling of the liquid with sulphur in flask *B* not only entirely prevents the presence of free lime in the final solution, but it tends to raise the $(S_M+S_P)/S_M$ ratio, although not in a very marked degree. In the following pairs of experiments the compositions are calculated back to the same CaO contents from the dilutions used for actual analysis.

TABLE II.

Expt. No.	Series.	Sulphur in solution. Total per cent.	Mono-sulphide per cent.	Poly-sulphide per cent.	Thio-sulphate per cent.	Total CaO per cent.	Ratio $(S_M+S_P)/S_M$.	Ratio S/CaO.
a.	1st flask ...	6·31	1·10	3·99	1·22	3·00	4·63	2·10
6, b.	Both flasks	6·71	1·08	4·34	1·28	3·00	5·02	2·24
7, a.	1st flask ...	4·05	0·54	2·01	1·50	1·88	4·72	2·15
b.	Both flasks	4·30	0·61	2·46	1·21	1·88	5·03	2·30

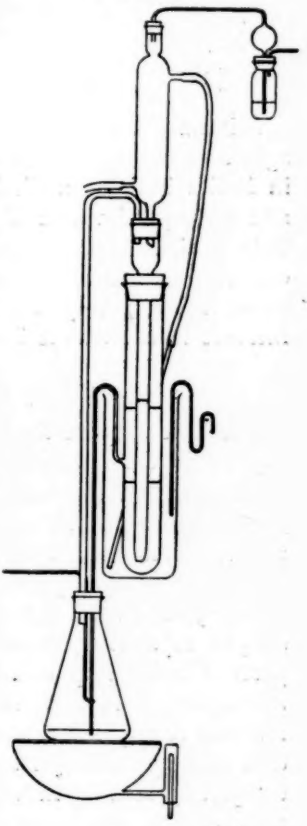
Removal of Hydrogen Sulphide from the Polysulphide Solution.

The continued passage of purified hydrogen or nitrogen through the polysulphide liquid removes appreciable quantities of hydrogen sulphide even at the ordinary temperature. At higher temperatures the evolution of hydrogen sulphide increases, and by boiling the liquid it is possible completely to destroy the polysulphides. This effect is in no way due to oxidation or decomposition by carbon dioxide, since it occurs in an atmosphere of inert gas, and after all dissolved gases have been removed from the solution. Since the decomposition is, then, solely indicative of the hydrolysis of the polysulphides, attempts have been made to measure the rate of evolution of hydrogen sulphide, in order, if possible, to detect the existence of more stable complexes. These attempts failed, and a description of the experimental methods need not be given. It may be noted, however, that after the polysulphides had been decomposed the residual liquid (which had been maintained at its original volume) contained only small quantities of free sulphur, a large quantity of thiosulphate, and but mere traces of calcium

sulphate. These points have, of course, bearing on the practical preparation of the lime–sulphur wash.

When, conversely, excess of hydrogen sulphide is passed into the lime–sulphur liquid, decolorisation again takes place, with the liberation of free sulphur and formation of calcium hydrosulphide (compare Divers and Shimidzu, *loc. cit.*, p. 282).

FIG. 2



Extraction of Sulphur from the Polysulphide Solution.

Preliminary experiments showed that, even in the total absence of air or oxygen, sulphur is continually removed from the polysulphide solution by agitation with sulphur solvents. Attention was given, therefore, to the rate of removal of the sulphur, in order to detect, if possible, the existence of more stable calcium polysulphides. The extraction apparatus used is shown in Fig. 2, which sufficiently explains its action. The apparatus worked satisfactorily with benzene. Apart from the fact that a special apparatus was required for solvents heavier than the solution, it was found that chloroform was a very unsatisfactory agent, whilst carbon disulphide could not be used owing to the formation of thiocarbonates.

During the course of an experiment the polysulphide liquid and the purified benzene came in contact only with pure nitrogen. The sulphur removed was estimated, after evaporating the benzene, by oxidising it in solution in 20 per cent. sodium hydroxide with sodium peroxide.

The following results (Expt. 8) are typical of a series. The lime–sulphur solution used was that of Expt. 7*b* (table II).

TABLE III.

Time of extraction in hours.	Grams of polysulphide sulphur present.	Grams of sulphur removed.	Sulphur removed (total) per cent.	Sulphur removed (fraction) per cent.
Nil	0·2524	—	—	—
7·0	0·1893	0·0631	25·0	25·0
13·0	0·1326	0·1198	47·5	29·9
21·0	0·0841	0·1683	66·7	*36·5*
27·0	0·0565	0·1959	77·7	*32·8*
32·7	0·0398	0·2126	84·3	*29·5*
41·2	0·0231	0·2293	90·9	41·9
47·2	0·0110	0·2414	95·7	52·3

Column 5 represents the sulphur removed calculated as percentages of the amount left in solution at any one time. The figures in italics indicate a distinctly slower rate of removal of sulphur, and correspond with ratios of $(S_M+S_F)/S_M$ between 1·63 and 2·31. This is significant, although, as already stated, too much weight cannot be attached to these experiments by themselves. It is not clear, indeed, why the fractions removed should subsequently increase to the extent indicated by the curve.

Extraction of Sulphur from the Dried Product.

The lime-sulphur liquid in these experiments was evaporated to dryness in the absence of air. This was accomplished in a desiccator (calcium chloride) originally filled with nitrogen, and into which the liquid was run through siphon *c* (Fig. 1). The desiccator was then rendered vacuous, and arrangements made whereby any leakage allowed only purified nitrogen to enter the vessel.

The yellow solid left on drying contained quantities of needle-shaped crystals (probably calcium thiosulphate), but the major portion was amorphous. The whole mass was broken up to facilitate desiccation, and the semi-crystalline material subsequently reduced to a powder, which was then spread out thinly in a glass dish and again subjected to the drying process. The powder was completely soluble in water. In the first extraction experiments pure carbon disulphide was poured over the powder, which was macerated with a light pestle under the surface of the liquid. The latter was then poured off, and the operation repeated. This extraction process was carried out at intervals over three months, and small but distinct quantities of sulphur were still being removed. The solid residue was then dried in a vacuum, and a yellow mixture of crystalline and indeterminate-shaped material again obtained. This solid was completely soluble in water, and the yellow solution precipitable by acids, so that it still contained polysulphide material. The solution was analysed (Expt. 9), and the $(S_M+S_r)/S_M$ ratio calculated. This was 1·40. That of the original liquid (Expt. 2) was 4·30.

In all subsequent experiments the dried polysulphide material was mixed with extracted silver sand, and extracted with carbon disulphide in a thimble in the special apparatus already described (Fig. 2). This reduced the possibility of hydrolysis or other secondary decomposition to a minimum, both by reducing the time of extraction and by preventing any possible access of air. By the construction of the apparatus the solid was always covered with a deep layer of pure carbon disulphide. In these experiments it was necessary to cool the extraction tube with a stream of water. One typical experiment will be quoted in detail (Expt. 10).

TABLE IV.

Weight of dried substance = 3 grams.

Time of extraction. Hours.	Weight of sulphur removed. Gram.
3·0	0·0321
3·8	0·0933
2·0	—
3·5	0·0460
4·0	0·0140
4·0	0·0008

The solid was removed from the cartridge, dried, and dissolved in water, and made up to 500 c.c. The solution was deep yellow, and contained polysulphide. On adding $N/10$-hydrochloric acid no precipitation was caused at first (compare Expt. 18), the acid thus taken up being much greater than with the ordinary polysulphide solution. Three grams of the original dry material were also dissolved in water and made up to 500 c.c. The results of the examination of both materials were as follows:

TABLE V.

Material.	Sulphur in solution. Total per cent.	Mono-sulphide per cent.	Poly-sulphide per cent.	Thio-sulphate per cent.	Total CaO per cent.	Ratio $(S_M+S_P)/S_M$.
Dry non-extracted ...	51·0	6·9	27·1	14·5	25·1	4·93
Dry extracted (calculated on original amount)	26·3	6·3	3·16*	5·4†	26·2	1·51
Original Liquid		See Expt. 5.				4·90

* For the estimation of these small quantities of polysulphides the liquid is titrated with iodine solution to apparent disappearance of the colour. The reaction $CaSx+I_2=CaI_2xS$ is completed before the thiosulphate is attacked (compare Harris, *Expt. Stat. Mich. Tech. Bull.*, Jan. 1911).

† This reduction in the amount of thiosulphate sulphur is due to the formation of calcium sulphate, etc.

Attempted Preparation of Calcium Disulphide.

The compound $CaS_2,3H_2O$ is stated (see above) to be produced in the form of yellow crusts when lime and sulphur are boiled together and the mixture is filtered hot. It is certainly not obtainable when excess of sulphur is employed, so attempts have been made with the quantities calculated from the equation:

$$3Ca(OH)_2 + 6S = CaS_2O_3 + 2CaS_2 + 3H_2O,$$

namely, 56 grams of quicklime and 64 grams of sulphur, and also with slightly larger and with slightly smaller amounts of sulphur. In two cases where the above quantities of sulphur and lime were boiled with 1 litre of water for two hours and filtered hot, the operations being conducted in the absence of air, the liquids obtained gave the following analytical results:

TABLE VI.

	Expt. 11.	Expt. 12.
$S_M + S_P$	1·55%	1·80%
S_P	1·24	1·50
S_M	0·31	0·39
S as thiosulphate	0·50	0·62
$(S_M + S_P)/S_M$	5·0	4·8

TABLE VIII.

Normality of HCl	Expt 18. C.c. required for permanent turbidity.
0·002	152·0
0·005	48·7
0·01	21·5
0·02	4·8
0·05	1·9

After a day or two the liquids deposited yellow, prismatic crystals with sharp ends. These proved to be oxysulphides. They were, in fact, identical with Herschell's crystals. Similar results were obtained in other experiments. In no case was a crystalline polysulphide obtained by this method.

Composition of Herschell's Crystals.

Herschell's crystals were prepared by a method similar to Geuther's except that all operations were carried out under rigid exclusion of air.

As already pointed out, elementary analysis alone shows very little difference between the formulæ assigned by Schöne, by Geuther, and in the present communication, as will be seen from the following:

	$3CaO,CaS_4,12H_2O$.	$2CaO,CaS_3,10H_2O$.	$CaS_3,CaO,7H_2O$.
Ca	28·98	28·03	27·97 per cent.
S	23·18	22·43	22·37 ,,
H_2O	39·13	42·05	44·05 ,,

Schöne's analyses must be regarded with a certain amount of suspicion, as he washed his product with water. Geuther, on the

other hand, does not state his method of estimating the water of crystallisation, the most important of the elementary figures.

In the following analyses, which are less complete than desirable (owing to the present suspension of the work), the water was estimated by ignition in a combustion tube packed with fused lead chromate. The analyses represent four different preparations; all of these are first crops of crystals, as later crops appeared to differ somewhat in composition.

TABLE VII.

Expt. No.	Ca. per cent.	H_2O per cent.	Sulphur. Total per cent.	Sulphur. Poly-sulphide per cent.	Sulphur. Mono-sulphide per cent.	Ratio. $(S_m+S_r)/S_m$.
13	27·88	43·85	—	—	—	—
14	28·10	—	22·13	—	—	—
15	—	44·14	21·49	10·56	10·93	1·97
16	—	—	21·76	10·85	10·91	1·99
17	—	—	23·92*	10·82	10·81	2·00

* This preparation contained 2·29 per cent. of sulphur in the form of thiosulphate, probably owing to the concentration having been carried too far.

Action of Dilute Acids on the Polysulphide Solution.

When very dilute hydrochloric acid, for example, $N/500$, is run into the lime–sulphur solution, there is a lengthy period of non-precipitation of sulphur, and a considerable volume of acid can be added without any apparent effect being produced. With $N/100$- and $N/10$-hydrochloric acid, added drop by drop, it can be seen that sulphur is at once precipitated and at first re-dissolves; only when an excess of acid has been added is the opalescence, due to the separation of sulphur, quite permanent. Warming hastens the re-dissolving of the originally precipitated sulphur. The more dilute the acid employed, the greater the total amount of acid which can be added. Thus, to quantities of 50 c.c. of the lime–sulphur solution from Expt. 5 diluted to ten times its volume, the amounts of hydrochloric acid shown in table VIII were added at 18° to produce permanent turbidity.

This effect may be caused (1) by the formation of high polysulphides of hydrogen which take time to decompose and are more stable in the strongly alkaline solutions (compare Schenk and Falcke, *loc. cit.*):

$$CaS_5 + 2HCl = H_2S_5 + CaCl_2 \text{ and}$$
$$H_2S_5 = H_2S + 4S,$$

or (2) by the re-attachment of the sulphur first liberated (probably as colloid) thus:

$$CaS_5 + 2HCl = H_2S + CaCl_2 + 4S,$$
$$xCaS_5 + 4S = xCaS_{5+4/x}$$

and, since no hydrogen sulphide appears to be liberated,

$$CaS_5 + H_2S = Ca(SH)_2 + 4S,$$

the sulphur re-dissolving as before. It is possible, of course, that the sulphur actually re-dissolves in the polysulphide solution, either wholly or in part, in non-chemical form. Indeed, the partly acidified solutions deposit sulphur more rapidly on the addition of an electrolyte, for example, sodium chloride; ordinary precipitation may therefore be deferred until an electrolyte (calcium chloride) is accumulated in sufficient concentration.

At the higher concentrations of hydrochloric acid there is produced an almost immediate turbidity which, however, clears after a few seconds if the reaction is not complete, or increases in intensity if the maximum amount of acid has been added.

If the effect is due to the formation of hydrogen polysulphides, it should be more marked at lower temperatures, at which these compounds are more stable. The reverse is the case, and much more acid may be added at the higher temperatures than at the lower.

In the experiments quoted in the following table the acid was run in drop by drop, and the solution, which was stirred continuously, was illuminated by a strong beam of light. The titrations at 0° and 1° are approximate, since at these temperatures the amount of acid added largely depends on the rate of addition. The more rapid the addition the more acid can be run in. In this case the sulphur separates suddenly as in the addition of acid to thiosulphate solutions. All results quoted are the mean of several observations. The materials and quantities used were those stated above (table VIII).

TABLE IX.

Expt. 19.

Temperature.	Normality of HCl.	C.c. of acid used.	Equivalent of acid. $\times 10^{-5}$.
1	0·005	58·0	*29·0*
9	0·005	27·8	13·9
18	0·005	48·7	24·3
0	0·01	18·0	*18·0*
9	0·01	11·6	11·6
18	0·01	21·4	21·4
32	0·01	27·4	27·4
60	0·01	35·8	35·8
75	0·01	46·4	46·4
86	0·01	55·0	55·0
93	0·01	59·9	59·9
0	0·02	—	—
9	0·02	2·5	5·0
18	0·02	4·8	9·6
35	0·02	7·5	15·0
60	0·02	14·5	29·0
75	0·02	21·5	43·0
87	0·02	26·0	52·0
93	0·02	29·2	58·4
18	0·05	1·9	9·5

The figures in italics (column 4) probably represent the formation, to a certain extent, of hydrogen polysulphides.

Assuming that the equations quoted above for the action of the dilute acid are correct, then taking the figures for 0·01*N*-hydrochloric acid at 93°, we get:

$0{\cdot}01N/HCl = 0{\cdot}00197$ gram $CaS_{4\cdot9}$ per c.c.
$= 0{\cdot}00125$ gram polysulphide sulphur per c.c.

The original content of 100 c.c. of the solution = 1·281 grams $CaS_{4\cdot9}$. After addition of acid, content of 100 c.c. = 1·053 grams $CaS_{4\cdot9}$ + 0·146 gram S, that is, the final solution contains 0·214 gram Ca + 0·985 gram S. The ratio of calcium to sulphur present as polysulphide is therefore:

$$\frac{0{\cdot}985}{32} \Big/ \frac{0{\cdot}214}{40} = 6{\cdot}1.$$

This implies the presence in solution of at least CaS_7.

Summary.

In the absence of air, lime and sulphur react in aqueous solution with the formation only of calcium polysulphides (or oxysulphides) and calcium thiosulphate.

When an excess of sulphur is used the ratio of $(S_M + S_P)/S_M$ usually lies between 4·5 and 5·0, but may exceed the latter figure under certain conditions.

Much of the sulphur of the higher polysulphides is loosely combined, and may be extracted both from solution and from the solid. Evidence is thus obtained of the probable existence of a stable CaS_2 complex. Calcium disulphide is probably not formed as such by the interaction of lime and sulphur.

The formula $CaS_2,CaO,7H_2O$ is suggested for Herschell's crystals.

The formation of the polysulphides from lime and sulphur may probably be expressed by the equations:

$$5Ca(OH)_2 + 6S = 2CaS_2,CaO + CaS_2O_3 + 5H_2O,$$
$$CaS_2,CaO + xS + H_2O = CaS_{x+2} + Ca(OH)_2.$$

By obtaining the re-dissolution of precipitated sulphur in the polysulphide solution, evidence can be obtained indicating the possible existence of polysulphides at least as high as CaS_7.

It is suggested that the polysulphides of calcium possess the constitution $Ca\langle{}^{S}_{S}\rangle S{:}S{:}S$ . . ., the atoms of sulphur in the chain becoming progressively more loosely attached.

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LVIII.—*The Absorption Spectra of Various Halogen and Nitrile Derivatives of Benzene and Toluene as Vapours and in Solution.*

By John Edward Purvis.

The author has described and discussed in earlier communications the absorption spectra of the vapours and solutions of various halogen derivatives of benzene and toluene (T., 1911, **99**, 811, 1699, 2318). It was proved, amongst other phenomena, that the iodine derivatives had no selective absorption in the ultra-violet regions, whereas the corresponding chlorine and bromine compounds had a large number of vapour bands and a smaller number of solution bands.

Later investigations (Purvis and McCleland, T., 1913, **103**, 1088; Purvis, *ibid.*, p. 1638) showed that the iodoanilines, *p*-iodophenol, the nitrobenzenes, the nitrotoluenes, *o*-nitrophenol, *o*-nitroanisole, *o*-nitroaniline, and the nitrobenzaldehydes had none of the numerous vapour bands found in benzene, toluene, aniline, phenol, and benzaldehyde. It was also shown that the finer vapour bands were eliminated as the number of chlorine or bromine atoms in the nucleus increased; for example, in 2:4-dichloroaniline, and in 2:4:6-trichloro- and tribromo-phenols, the phenomena became comparable with the solution phenomena.

This communication describes the results obtained when other halogen and various nitrile derivatives of benzene and toluene were investigated, in order to see how far the absorption is affected (1) by the introduction in the benzene nucleus of the two dissimilar atoms of chlorine and bromine, as in the *o*-, *m*-, and *p*-chlorobromobenzenes, as compared with the dichloro- and dibromo-benzenes and with benzyl chloride, (2) by the introduction of the nitrile group, as in benzonitrile and the *o*-, *m*-, and *p*-toluonitriles, as compared with phenylacetonitrile; and (3) by the total replacement of the hydrogen atoms in the nucleus as in hexachlorobenzene and hexamethylbenzene, or by the addition of six atoms of chlorine as in hexachloro*cyclo*hexane.

The substances examined were *p*-dichloro- and *p*-dibromo-benzenes, *o*-, *m*-, and *p*-chlorobromobenzenes, benzonitrile, *o*-, *m*-, and *p*-toluonitriles, hexachlorobenzene, hexamethylbenzene, hexachloro*cyclo*hexane, phenylacetonitrile, benzyl chloride, and benzyl alcohol.

It may be recalled that Baly (T., 1911, **99**, 856) re-investigated the absorption spectra of solutions of chlorobenzene, the dichlorobenzenes, and the chlorotoluenes.

The experimental methods have been described before.

p-*Dichlorobenzene.*—Baly (*loc. cit.*) has shown that the substance has five solution bands, the most refrangible of which is very weak, and that *o*- and *m*-dichlorobenzenes have only four.

The vapour of the substance was examined in a 200 mm. tube at temperatures and pressures varying from 40° and 767 mm. to 70° and 827 mm. At the former temperature there appeared eighty-one bands, which have been measured and classified. These bands can be separated into a series of groups of varying intensities, the most refrangible constituent of each of which is the strongest. The following numbers give the position of the heads of the more outstanding groups:

λ	Intensity.	No. of bands	λ	Intensity.	No. of bands
2847	Moderately strong.....	8	2692	Fairly strong	6
2798	Strong.....	16	2665	Fairly strong	7
2767	Moderately strong.....	12	2640	Fairly strong	5
2740	Moderately strong.....	8	2591	Moderately weak	3
2716	Strong.....	10	2546	Moderately weak	6

It is of some importance to note that several of these groups can be correlated with four of the solution bands described by Baly, for example:

Solution bands	2808	2731	2683	2580
Vapour bands	2798	2716	2665	2546

Solution not only causes a closing up of the separate constituents, but also shifts the bands more towards the red.

p-*Dibromobenzene.*—The alcoholic solution (Fig. 1) showed three well-marked bands and a doubtful one at about 1/λ 3859 (λ 2590). There does not appear to be a well-marked band beyond this, but the somewhat rapid absorption to about 1/λ 4000 (λ 2498) may indicate a widening out of a very diffuse band. The bands are much weaker than the corresponding bands of *p*-dichlorobenzene, and they are shifted a little more towards the red. The rapid step-out of the line of general absorption between 1/λ 4200 (λ 2380) and 1/λ 4660 (λ 2142) may indicate a large band which extends into the Schumann region, for a similar phenomenon was observed in *p*-dichlorobenzene in a *N*/10,000-solution, although it was not so well marked.

The vapour of the substance was examined in a 200 mm. tube at temperatures and pressures varying between 70° and 827 mm. and 120° and 927 mm. The number of bands observed was thirty-one, and these have all been measured and classified. Like the bands in the vapour of *p*-dichlorobenzene, they can be arranged in a series of groups of varying degrees of intensity. The following

numbers give the position of the bands of the stronger groups, together with the positions of the corresponding three stronger solution bands:

Solution bands.	Vapour bands.		
λ.	λ.	Intensity.	No. of bands.
2835	2808	moderately strong	8
	2788	moderately weak.....	8
2740	2728	moderately strong	5
	2724–2714	moderately weak wide band, which shows doubtful signs of division.	
	2700	moderately weak.....	4
2655	2625	moderately strong	5

A comparison of the vapour bands of *p*-dichloro- and *p*-dibromobenzenes showed that, generally speaking, they appeared to be more diffuse and wider in *p*-dibromobenzene and were fewer in number.

Some of the bands in both substances occurred in groups of three, the most refrangible constituent of each of which was the strongest. These triplets are more frequent in *p*-dichlorobenzene. The following groups of triplets in the two compounds are fairly comparable in appearance: the numbers give the wave-lengths of the most refrangible constituent:

p-dichlorobenzene ...	2798	2790	2783
p-dibromobenzene.....	2808	2795	2788

These three groups of triplets are not unlike the groups found in *p*-dichlorobenzene at 2835, 2827, 2818, 2811.

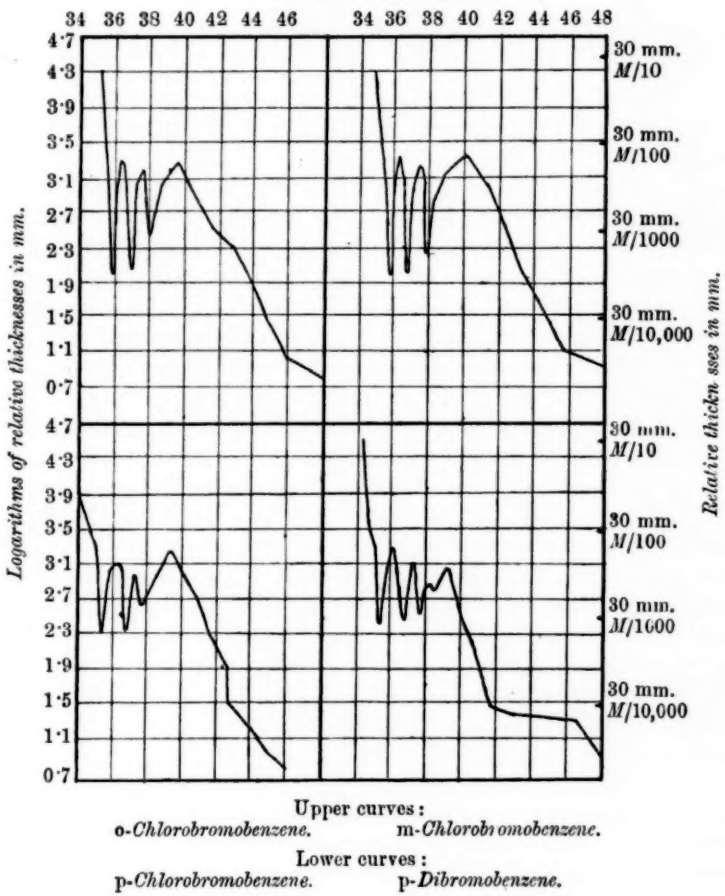
The differences in the solution and the vapour phenomena are exactly like the differences observed with substances previously examined, in that all the vapour bands disappear in solution and are replaced by a few wide diffuse bands. The marked difference between the absorption phenomena of the isomeric substances is also noteworthy. As the temperature and the pressure increase, the vapour bands widen into each other in such a manner that the phenomena become comparable with those observed in solution, the chief difference being one of position.

o-, m-, and p-*Chlorobromobenzenes.*—The alcoholic solutions (Fig. 1) showed three well-marked bands. The bands of the ortho- and meta-compounds are more comparable in appearance with one another than with those of the para-compounds. The bands of the meta-compound are a trifle stronger than those of the ortho-compound, and are shifted a little more towards the red end. The bands of the para-compound are shifted still more towards the red, and are slightly wider and more diffuse; the most refrangible band is very weak and diffuse as compared with the corresponding

band of the ortho- and meta-compounds. The rapid widening of the most refrangible band of all the three compounds is also noteworthy, for it may indicate traces of other bands.

The vapour of *o*-chlorobromobenzene was examined at temperatures and pressures ranging between 50° and 762 mm. and 90°

FIG. 1.



and 842 mm. The total number of bands observed was sixty, and they could be separated and classified into various groups or series of groups. The following numbers give the position of the strongest and most refrangible constituent or head of three outstanding groups and the position of the heads of the corresponding single solution bands:

	Solution bands.	Vapour bands.		
	λ.	λ.	Intensity.	No. of bands.
o-C_6H_4ClBr	2785	2765	very strong	16
	2700	2685	very strong	19
	2630	2623	moderately strong	14
m-C_6H_4ClBr	2790	2770	strong	15
	2710	2690	strong	17
	2640	2622	moderately strong	11
p-C_6H_4ClBr	2825	2800	strong	17
	2730	2720	moderately strong	7
	2650	2632–2620	a diffuse band which shows doubtful signs of division.	

The vapour of *m*-chlorobromobenzene was examined between 50° and 762 mm. and 90° and 842 mm. The total number of bands observed was fifty-five, and these also could be divided into various groups. The numbers in the table give the position of the bands of the larger groups and the corresponding single solution bands:

The vapour of *p*-chlorobromobenzene was examined at similar temperatures and pressures, and ninety-eight bands were measured and classified. In the preceding table three of the groups of bands are compared with three corresponding solution bands.

The vapour bands of *o*- and *m*-chlorobromobenzene have a closer similarity to one another than to those of the para-compound. For example, each of a group of bands the heads of which in the ortho-compound are at 2765, 2685, 2623, has a similar appearance to the groups at 2770, 2690, 2622 in the meta-compound.

In the para-compound there are groups of bands which are different from any noticed in the ortho- and meta-compounds. In these instances the constituents of each group are much closer together, and tend to produce a series of wide diffuse bands; one outstanding group of the para-compound at 2800 is quite comparable with the groups 2765 and 2770 of the ortho- and meta-compounds. It is also noteworthy that the three outstanding groups of the ortho-compound at 2765, 2685, 2623, and of the meta-compound at 2770, 2690, 2622 are not unlike the groups of bands the heads of which in chlorobenzene are at 2698 and 2661, and in bromobenzene at 2707 and 2666 (*loc. cit.*).

The chief groups of the meta-compound are also not unlike those of *m*-dichlorobenzene (*loc. cit.*) except that the bands of the latter are shifted more towards the red end. Similarly, group 2765 of the ortho-compound compares well in appearance with group 2760 of *o*-dichlorobenzene, and, to a more doubtful extent, group 2685 of the former compound compares with group 2682 of the latter (*loc. cit.*), but there is a greater shift towards the red end in the case of *o*-chlorobromobenzene. Similar comparisons extend to the groups in *o*-dibromobenzene, but the bands of the latter are

shifted more towards the red. Also, the chief groups in *m*-chlorobromobenzene are not unlike those of *m*-dichlorobenzene, except that the former are shifted more toward the red, and are also like those of *m*-dibromobenzene, but the latter again are shifted more towards the red end.

The following groups of bands in *p*-chlorobromobenzene and *p*-dichlorobenzene are fairly comparable. The numbers are the wave-lengths of the more refrangible constituent of each group:

p-chlorobromobenzene	2800	2720	2704	2697	2682	2649	2636	2620	2549
p-dichlorobenzene	2811	2734	2716	2703	2686	2653	2640	2627	2546

The following groups of bands in *p*-chlorobromobenzene and *p*-dibromobenzene are also comparable in general appearance:

p-chlorobromobenzene	2800	2720	2704	2691
p-dibromobenzene	2808	2728	2714	2694

The differences in the solution and the vapour phenomena are again exactly like the differences observed in other substances (*loc. cit.*), namely, that, as the temperature and the pressure are increased, the bands widen into each other; gradually the numerous vapour bands disappear, and are replaced by a few diffuse wide bands. It is important to notice, too, that, as in the dibromobenzenes, there is a considerable number of vapour bands in the chlorobromobenzenes. There has been no elimination of these bands like that observed in the iodobenzenes previously investigated (*loc. cit.*).

Benzonitrile.—The solution curve (Fig. 3) shows three bands; the rapid widening of the most refrangible band on the more refrangible side may indicate the presence of other very weak bands. The rapid step-out of the line between $1/\lambda\,4400$ and $1/\lambda\,4700$ ($\lambda\,2270$ and $\lambda\,2130$) may also indicate the presence of a large band which extends into the Schumann region. It has been shown by Baly (*loc. cit.*), and the author has confirmed this observation, that chlorobenzene has seven solution bands, the most refrangible of which is extremely weak. The position of the benzonitrile bands is shifted much more towards the red end, and they are also stronger than the bands of chlorobenzene. The introduction of the nitrile group, therefore, has modified the absorption very considerably.

The vapour of benzonitrile was examined at temperatures and pressures varying between 50° and 852 mm. and 100° and 952 mm. There were fifty-three bands observed, and these have been measured and classified into various groups and series. The following numbers give the heads of three of the more outstanding groups, together with the head of the corresponding solution band.

	Solution band.	Vapour band.		
	λ.	λ.	Intensity.	No. of bands.
C_6H_5·CN	2785	2738	strong	13
	2710	2687	strong	11
	2640 ?	2614 to 2604	wide diffuse band.	
o-C_6H_4Me·CN	2850	2796	strong	8
	2780	2719	moderately strong.....	11
	2700	2692 to 2628	a series of weak bands.	
m-C_6H_4Me·CN	2840	2794	strong	7
	2776	2718	fairly strong	11
	2740	2710 to 2696	a series of weak bands.	
p-C_6H_4Me·CN	2790	2761	fairly strong	7
	2730	2702	fairly strong	16
	2710	2666	fairly strong	11

The series of bands the head of which is at λ 2738 in benzonitrile compare fairly well in appearance with a group of bands of chlorobenzene described previously (*loc. cit.*), the head of which is at λ 2698, and the series, the head of which is at λ 2687, is comparable with the group of chlorobenzene at λ 2661.

The position of the bands as compared with those of aniline (Purvis, T., 1910, **97**, 1546) also shows that there has been a considerable shift of the solution bands and of the vapour bands towards the red.

The general results are similar to those of other substances in that all the vapour bands are replaced by a few solution bands, and, as the temperature and the pressure increase, widen into each other, and the phenomena gradually become comparable with the solution phenomena.

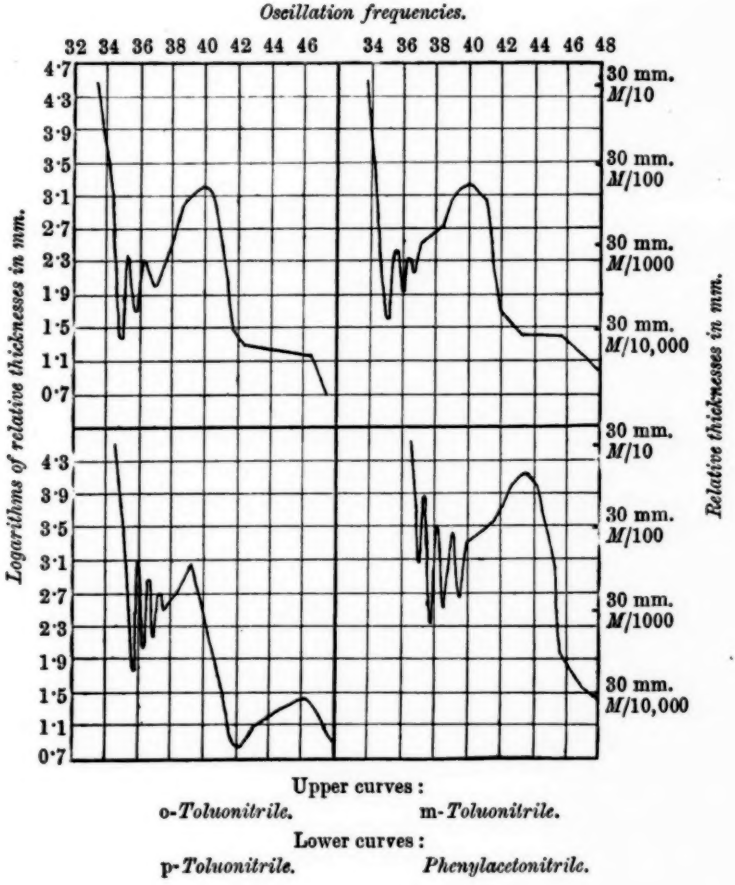
o-, m-, and p-*Toluonitriles.*—The solution curves (Fig. 2) show that in the ortho-compound there are three bands the most refrangible of which widen out on the more refrangible side; that in the meta-compound there are also three bands, whereas in the para-compound there are indications of a weak fourth band. Besides these somewhat narrow diffuse bands there are indications of a large band in the ortho- and meta-compounds on the more refrangible side and extending into the Schumann region. This band, in the para-compound, is fairly well marked, as shown by the curve. The least refrangible band of the first three of the para-compound is much sharper than the corresponding band in the ortho- and meta-compounds; the latter are very diffuse. It is also noteworthy that the toluonitrile bands are much weaker than the benzonitrile bands (Fig. 3), but the least refrangible band of *p*-toluonitrile compares well with that of benzonitrile in intensity.

The vapours of the three substances were examined in a 200 mm. tube at temperatures and pressures ranging from 16° and 755 mm. to 100° and 922 mm. In the case of the ortho-compound the

number of bands observed was thirty-three, which have been measured and classified. The numbers in the table give the position of the more outstanding groups compared with the corresponding solution bands.

The vapour of *m*-toluonitrile was examined from 17° and 755 mm. to 100° and 910 mm., and thirty-seven bands were observed and

FIG. 2.



measured. The numbers in the table compare the corresponding groups of the solution bands.

The vapour of *p*-toluonitrile was examined between 15° and 749 mm. and 110° and 1010 mm., and thirty-seven bands were observed and measured. The numbers in the preceding table compare the chief groups with the solution bands.

The large solution band in the extreme ultra-violet region appears also in the vapours of the three compounds, and it is especially well marked in the vapour of the para-compound. It does not break up into a series of finer bands, although there is a weaker diffuse band on its less refrangible side.

There is a closer resemblance between various groups of the vapour bands in the ortho- and meta-compounds than appears in the para-compound; but the following groups of bands in all three compounds, and a group of bands in benzonitrile, are fairly comparable. The numbers represent the heads of the constituent band on the more refrangible side:

o-toluonitrile	2796	2719	2703
m-toluonitrile.....	2794	2718	2696
p-toluonitrile	2761	2721	2713
benzonitrile	2738	—	—

Again, the group of bands at 2796 in *o*-toluonitrile is comparable with the group at 2714 in *o*-chlorobenzene, and with the group at 2732 in *m*-chlorobenzene described previously (*loc. cit.*). At the same time it should be clearly understood that no exact comparison of all these various vapour bands was attempted. Such a definite comparison would mean that the radiant energy should have passed through the same number of molecules, and that the dispersion should be greater than was employed. Neither of these conditions is implied in the description of the observed phenomena.

The differences in the solution and the vapour phenomena of benzonitrile and of the three toluonitriles are again like those observed in other substances described previously (*loc. cit.*) in that all the numerous vapour bands disappear in solution and are replaced by a few wide, diffuse bands; that the isomeric substances show differences amongst themselves; and that the vapour bands gradually widen into each other as the temperature and the pressure increase, and the phenomena then become not unlike the solution phenomena.

Phenylacetonitrile.—The solution curve (Fig. 2) shows four well-marked bands, and the rapid step-out of the rays between $1/\lambda\,4000$ and $1/\lambda\,4150$ ($\lambda\,2498$—$\lambda\,2408$) probably indicates one or more very weak, diffuse bands which widen into each other. It is important to notice that the bands are weaker than the three bands of benzonitrile, and that the latter are shifted more towards the red end. The introduction of the cyanogen group in the aliphatic side-chain has enabled the benzene nucleus to regain, in some measure, the characteristic benzene solution bands.

The comparatively high boiling point of phenylacetonitrile made it difficult to examine the vapour of the substance, but in a

200 mm. tube at various temperatures and at 767 mm. pressure the following phenomena were observed:

90° Very doubtful absorption between λ2640 and λ2620, between 2565 and λ2550, and between λ2520 and λ2500; the rays were then transmitted to λ2200.

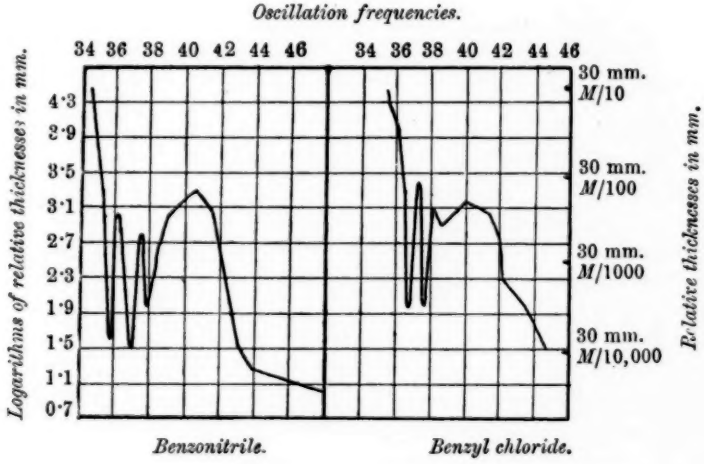
120° Rays were feebly absorbed between λ2640 and λ2620, between λ2565 and λ2550, and between λ2520 and λ2500; then transmitted to about λ2270.

130° The rays were absorbed between λ2660 and λ2620, between λ2565 and λ2550; then feebly transmitted to λ2510.

150° The rays were absorbed from about λ2670, but Cd. 2573 was just visible.

It appears, therefore, that the cyanogen group has destroyed the twenty-two narrow vapour bands of toluene described by

FIG. 3.



Hartley (*Phil. Trans.*, 1907, [A], **208**, 475), and that the solution and the vapour phenomena are fairly comparable.

Benzyl Chloride.—The solution curve (Fig. 3) shows two moderately strong bands and a very weak one on the more refrangible side. Baly and Collie (T., 1905, **87**, 1332) describe three solution bands of the substance. These bands are much weaker than the phenylacetonitrile bands, and also much weaker than the toluene bands.

The easy decomposition of this substance made the observations of the absorption spectra of the vapour very difficult, but the following phenomena were observed when the vapour was at various temperatures and pressures:

60° and 806 mm. The rays were feebly absorbed between λ2700 and λ2695; between λ2660 and λ2640, between λ2600 and λ2590, and then transmitted to λ2310.

75° and 836 mm. Rays were fairly well absorbed between λ2710 and λ2695 (Cd. line 2573 well marked), and then absorbed to about λ2520. From here, to about λ2420, the rays were very feebly transmitted.

90° and 866 mm. The rays were absorbed from λ2720.

As in phenylacetonitrile, there were no vapour bands like those found in toluene or in the chlorotoluenes (*loc. cit.*).

These two substances were also compared with benzyl alcohol, and the vapour of the latter substance showed the following phenomena:

t°	Pressure in mm.	
75	836	The rays showed doubtful signs of weakening between λ2650 and λ2625; and were then transmitted to λ2420.
90	866	The rays showed very feeble absorption between λ2650 and λ2620, between λ2560 and λ2550, and were then feebly transmitted to λ2470.

In benzyl alcohol, therefore, all the vapour bands of toluene were absent. Benzyl alcohol is easily oxidised to the aldehyde, but the fact that no aldehyde bands were observed in the vapour showed that there had been no oxidation under the experimental conditions. The tube was always filled with nitrogen gas before the commencement of the experiments.

Hexachlorocyclohexane.—Hartley (T., 1881, **39**, 153) showed that alcoholic solutions did not exhibit bands, and were remarkably transparent. The author has repeated these experiments, and confirmed the observations. The following numbers give the position to which the rays are transmitted through various thicknesses of a *M*/100-solution in alcohol: 80 mm. to 2550 (but Cd 2313 was just visible); 70 mm. to 2480 (but Cd 2329, 2321, 2313 were just visible); 60 mm. to 2450 (but Cd 2329, 2321, 2313, and 2265 fairly well-marked); 50 mm. to 2270; 40 mm. to 2200; 30 mm. to 2200; 20 mm. to 2150; 10 mm. to 2144.

The comparatively feeble vapour pressure made the examination of the vapour of the substance difficult, but the following numbers give the positions to which the rays were transmitted in the 200 mm. tube at 747 mm. pressure and at various temperatures: At 150° the rays were transmitted to λ 2144; 160° to 2200; 170° to 2290; 180° to 2340; 190° to 2415; 200° to 2420. Like the solution, the vapour, so far as it was examined, showed no bands.

Hexachlorobenzene.—This substance is not very soluble, but an approximately *M*/1000 alcoholic solution was obtained. No bands were observed, and the following numbers give the positions to

which the rays were transmitted through various strengths and thicknesses:

M/1000, 90 mm. the rays were transmitted to λ 2770; 70 mm. to 2760; 60 mm. to 2750; 40 mm. to 2730; 30 mm. to 2690; 20 mm. to 2660; 10 mm. to 2590; 6 mm. to 2530.

M/10,000, 30 mm. the rays were transmitted to λ 2460; 20 mm. to 2450; 16 mm. to 2420; 14 mm. to 2280; 6 mm. to 2240.

The comparatively weak vapour pressure of the substance made the investigation of its vapour difficult, but the following numbers give the position to which the rays were transmitted in the 200 mm. tube and at 747 mm.: At 180° the rays were transmitted to λ 2350; 190° to 2430; 200° to 2520; 210° to 2570; 220° to 2630.

There were no bands of selective absorption in the vapour so far as it was examined, nor is it likely there would be at higher temperatures.

Hexamethylbenzene.—Solutions of the substance were examined, but no bands were seen. The following numbers give the positions to which the rays were transmitted through various strengths and thicknesses:

M/100, 60 mm. the rays were transmitted to λ 2450; 50 mm. to 2400; 40 mm. to 2390; 30 mm. to 2380; 20 mm. to 2360; 10 mm. to 2340.

M/1000, 30 mm. the rays were transmitted to λ 2310; 20 mm. to 2250; 10 mm. to 2200.

The vapour of the substance was not examined.

The well-known seven solution bands and the more numerous vapour bands of benzene have completely disappeared from the solutions and vapours of the last three substances. It is also evident that hexachloro*cyclo*hexane is much more transparent than hexachlorobenzene and hexamethylbenzene, and that hexamethylbenzene is more transparent than hexachlorobenzene.

General Results.

The chief results of the preceding observations are: (1) The considerable number of vapour bands in *p*-dichloro- and *p*-dibromobenzenes, in *o*-, *m*-, and *p*-chlorobromobenzenes, in benzonitrile, and in *o*-, *m*-, and *p*-toluonitriles, which disappear when the substances are in solution and are replaced by a few moderately wide, diffuse bands. (2) The marked differences in the absorption phenomena of the isomeric substances, especially in the para-compounds as compared with the ortho- and meta-compounds; these differences are more strongly marked in the vapours than in the solutions. (3) The absence of narrow vapour bands in phenylaceto-

nitrile, benzyl chloride, and benzyl alcohol. (4) The complete elimination of both vapour bands and solution bands in hexachloro*cyclo*hexane, hexachlorobenzene, and hexamethylbenzene. (5) The similarity of the vapour bands and the solution bands at the higher temperatures and pressures in those compounds which exhibit a series of finer vapour bands at the lower temperatures and pressures.

It has already been suggested (*loc. cit.*) that the fundamental vibrations of the atoms in a molecule are influenced by their type and nature as well as by their orientation and by the physical conditions of the system, and that the final adjustment of the oscillations producing selective absorption is controlled by these conditions as well as by the distribution and reaction of the vibrations produced by the radiant energy. This energy reacts differently on different atoms and atomic groups, and the oscillatory movements which determine the nature and extent of the absorption are modified by the interdependence and relationships of the various oscillatory centres.

It is considered that the absorption depends upon an influence inherent in the atom, which is electronic and, to a large extent, independent of the weight, but is controlled by the orientation and relationship with other atoms or groups, which also act as oscillatory centres. If the specific absorption depended solely on the weight, there should be no vapour bands in the dibromobenzenes, for these substances are heavier than iodobenzene, which shows no bands (*loc. cit.*). The argument will apply à fortiori to nitrobenzene, which has no fine vapour bands, and only traces of a weak solution band (*loc. cit.*). That each atom or group reacts on the vibrations of other groups according to its position is indicated by the different phenomena exhibited by the isomeric substances, and is further strengthened by the fact that phenylacetonitrile has more solution bands than the toluonitriles, and that the vapour bands of toluene are completely destroyed in phenylacetonitrile, whereas there is a considerable number of vapour bands in each of the toluonitriles.

It may be recalled that there are no fine vapour bands in substances containing two similar nuclei, such as diphenyl (Purvis, T., 1914, **105**, 590); all the numerous benzene vapour bands are wholly eliminated. Herein there is a strict comparison with the phenomena shown by hexachlorobenzene and hexachloro*cyclo*hexane; and, if valency is considered to have an electronic origin, the remarkable transparency of hexachloro*cyclo*hexane may be explained by assuming that the oscillations are damped by the chlorine atoms, whereas in hexachlorobenzene, which is not so

transparent, the valencies are still unsaturated to some extent. On the other hand, where it may be considered that the nuclei are not so closely connected as in diphenylmethane, the solution bands show (*loc. cit.*) that the oscillations have a freer movement, but not sufficiently free to produce the fine vapour bands. At the same time, the absence of the finer vapour bands in phenylacetonitrile, benzyl chloride, and benzyl alcohol is not explained by such a suggestion. It may be that the lengthening of the side-chain in these compounds by the added atoms or groups neutralises the fundamental oscillations of the nucleus by enabling them to react on the nucleus to such an extent that only a few diffuse bands are produced.

In the solutions, the external influence of the solvent modifies the oscillations, so that the number of individual bands is greatly decreased; it is noteworthy that the comparatively broad, diffuse solution bands can often be compared with various groups of the vapour bands. A group of vapour bands would seem to close up under the influence of the solvent to form a diffuse wide band, whereas in other instances the vapour bands are so weak that they practically disappear when the substance is in solution.

I desire to thank the Government Grant Committee of the Royal Society, by whose assistance the greater part of the cost of the research has been defrayed.

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CAMBRIDGE. [*Received, Jan. 28th*, 1915.]

LIX.—*The Action of Aldehydes on the Grignard Reagent. Part II.*

By JOSEPH MARSHALL.

WHEN an aldehyde (1 mol.) is added to a cold, ethereal solution of magnesium in an alkyl or aryl haloid, it is noticed that the precipitate which is formed on the addition of each drop of aldehyde is redissolved until about one-third of the whole has been added, after which the precipitate remains undissolved, and finally the ether is filled with a greyish, crystalline mass, which may be heated on the water-bath during several hours without undergoing any visible change. If, however, a further quantity of an aldehyde is added to the mixture, although only very little heat is developed, a considerable alteration in the character of the pre-

cipitate is observed, a heavy, brownish, viscous mass taking the place of the original crystalline precipitate. If, after some hours, the ether is poured away from the lower layer and is mixed with dilute acid, it is found that only a trace of the aldehyde is present, so that evidently combination has taken place between the aldehyde and the original product of the reaction. The products of the hydrolysis of the viscous mass by dilute acid are very different from that obtained by the decomposition of the original crystalline material.

It was shown in a previous paper (T., 1914, **105**, 527) that the products obtained by the action of benzaldehyde (2 mol.) on magnesium phenyl bromide (1 mol.) are benzophenone and benzyl alcohol. The reaction may be expressed by the equations:

$$C_6H_5\cdot CHO + C_6H_5\cdot MgBr = (C_6H_5)_2CH\cdot OMgBr,$$
$$(C_6H_5)_2CH\cdot OMgBr + C_6H_5\cdot CHO + H_2O = (C_6H_5)_2CO + C_6H_5\cdot CH_2\cdot OH + OH\cdot MgBr,$$

diphenylcarbinol being oxidised to benzophenone and benzaldehyde being reduced to benzyl alcohol.

It is of interest to note that Sabatier and Murat (*Compt. rend.*, 1913, **157**, 1496) state that the chief product of the reaction between benzaldehyde and magnesium phenyl bromide is tetraphenylethane, whilst diphenylcarbinol is produced only to the extent of 3 per cent., and is accompanied by diphenylmethane and benzophenone. These results are explained by assuming that a part of the diphenylcarbinol is reduced to tetraphenylethane and diphenylmethane at the expense of the remainder of the carbinol, which is converted into benzophenone.

In the light of the experiments recorded in the present paper, another explanation of the results of Sabatier and Murat is suggested. It is well known that a certain amount of diphenyl is produced in the reaction between magnesium and bromobenzene, and accordingly a small quantity of magnesium remains undissolved. If to the solution containing an excess of magnesium a quantity of benzaldehyde equivalent to the bromobenzene is added, it is evident that there is, in reality, an excess of the aldehyde, which will react with the magnesium diphenylcarbinyl bromide, and on hydrolysis a certain amount of benzophenone will be produced. During the hydrolysis, also, hydrogen is liberated, owing to the solution of the excess of magnesium, and it is probable that the reduction of diphenylcarbinol (or, more probably, magnesium diphenylcarbinyl bromide) to tetraphenylethane or diphenylmethane is effected by the hydrogen thus formed. In the experiments made by the author, any excess of metal was removed before the aldehyde was added, and in every such case the yield of

diphenylcarbinol (or benzophenone) was more than 50 per cent. of the total possible amount. In order to test the explanation of the results of Sabatier and Murat, suggested above, an experiment was made in which a large excess of magnesium was left in contact with the reaction mixture. The yield of tetraphenylethane in this experiment was 45 per cent., whilst the fraction containing diphenylcarbinol and benzophenone diminished to less than 10 per cent.

If a similar reaction occurs when a magnesium alkyl haloid is allowed to react with an excess of benzaldehyde, the products of the reaction should be a phenyl alkyl ketone and benzyl alcohol, and this has been found to be the case, for example, in the reaction between magnesium methyl iodide and an excess of benzaldehyde, benzyl alcohol and acetophenone have been isolated. Since acetophenone condenses with benzaldehyde, a further excess of benzaldehyde may lead to the formation of phenyl styryl ketone; this substance has also been isolated in the reaction. In the earlier paper (*loc. cit.*) it was stated that the crystalline compound obtained in this reaction was methyldeoxybenzoin, but there is no doubt that it is phenyl styryl ketone contaminated with a small quantity of dibenzoylmethane, from which it is only separated with difficulty. It may be pointed out that the relation between dibenzoylmethane and the hydrate of phenyl styryl ketone is the same as that between acetophenone and phenylmethylcarbinol.

A similar result was obtained when an excess of benzaldehyde was allowed to react with magnesium dimethylcarbinyl iodide, the chief product of the reaction being styryl methyl ketone.

The results obtained by the action of an excess of an aliphatic aldehyde on magnesium carbinyl haloids were similar to those already described in the case of benzaldehyde. Thus, when an excess of acetaldehyde was allowed to react with magnesium phenyl bromide, the substances isolated were acetophenone and benzoylacetone, formed according to the scheme:

$$C_6H_5\cdot CH(OMgBr)\cdot CH_3 \longrightarrow C_6H_5\cdot CO\cdot CH_3 \longrightarrow [C_6H_5\cdot CO\cdot CH_2\cdot CH(OH)\cdot CH_3] \longrightarrow C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

The whole of these results may be explained by the assumption that the excess of the aldehyde present in each experiment is capable of reacting as an oxidising agent, being itself reduced to a primary alcohol. Although aldehydes are usually regarded as reducing agents, the formation of benzoic acid from benzaldehyde in the presence of sodium hydroxide is a well-known example in which one molecule of the aldehyde behaves as an oxidising agent towards a second molecule. If the equation for this reaction is compared with an equation representing the oxidation of phenyl-

methylcarbinol to acetophenone by means of benzaldehyde, it will at once be noticed that the two are very similar:

$$C_6H_5\cdot CHO + C_6H_5\cdot CHO + H_2O = C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot CO_2H \quad . \quad . \quad . \quad . \quad (1)$$

$$C_6H_5\cdot CH(OH)\cdot CH_3 + C_6H_5\cdot CHO = C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot CO\cdot CH_3 \quad . \quad . \quad . \quad . \quad (2)$$

If the hydrate of benzaldehyde is written in each equation, the similarity between them is still more evident:

$$C_6H_5\cdot CH(OH)_2 + C_6H_5\cdot CH(OH)_2 = C_6H_5\cdot C(OH)_3 + C_6H_5\cdot CH_2\cdot OH \quad . \quad . \quad . \quad . \quad (3)$$

$$C_6H_5\cdot CH(OH)\cdot CH_3 + C_6H_5\cdot CH(OH)_2 = C_6H_5\cdot C(OH)_2\cdot CH_3 + C_6H_5\cdot CH_2\cdot OH \quad . \quad . \quad . \quad . \quad (4)$$

The assumption may therefore be made that any mechanism which explains the formation of benzoic acid from benzaldehyde will also account for the production of acetophenone from phenylmethylcarbinol.

It has been shown by Claisen (*Ber.*, 1887, **20**, 646) that when sodium methoxide is brought into contact with benzaldehyde, the first product of the reaction which can be isolated is the ortho-compound $C_6H_5\cdot C(ONa)(O\cdot CH_3)\cdot OCH_2\cdot C_6H_5$, which, by suitable means, may be converted into benzyl benzoate. Also, Kohn [Keane] and Trantom (T., 1899, **75**, 1155) have brought forward evidence which indicates the intermediate production of a similar compound when sodium hydroxide reacts with benzaldehyde. The suggestion is therefore made that in the reaction between benzaldehyde and magnesium phenylmethylcarbinyl bromide a similar ortho-derivative of acetophenone is produced, the two reactions being contrasted in (5) and (6):

$$C_6H_5\cdot CHO + C_6H_5\cdot CHO + NaOH = C_6H_5\cdot C(ONa)(OH)\cdot O\cdot C_7H_7 \quad . \quad . \quad . \quad . \quad (5)$$

$$C_6H_5\cdot CHO + C_6H_5\cdot CH(OMgBr)\cdot CH_3 = C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_3 \quad . \quad . \quad . \quad . \quad (6)$$

This substance may then condense with an excess of benzaldehyde, after which further oxidation may take place:

$$C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_3 + C_6H_5\cdot CHO = C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_2\cdot CH(OH)\cdot C_6H_5 \quad . \quad . \quad (7)$$

$$C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_2\cdot CH(OH)\cdot C_6H_5 + C_6H_5\cdot CHO = C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_2\cdot C(OH)(O\cdot C_7H_7)\cdot C_6H_5 \quad . \quad . \quad (8)$$

Finally, just as the benzoic acid derivative yields on hydrolysis benzyl alcohol and sodium benzoate, the derivative of acetophenone

is decomposed by the addition of water into benzyl alcohol and acetophenone:

$$C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_3 + H_2O = C_6H_5\cdot CO\cdot CH_3 + C_6H_5\cdot CH_2\cdot OH + MgBr\cdot OH \quad . \; . \; . \quad (9)$$

The fact that benzyl alcohol is not produced until the hydrolysis of the reaction product is effected is strong evidence in favour of the foregoing explanation of the reaction, for if benzyl alcohol were formed by the direct action of the aldehyde on the carbinyl haloid, it should be found dissolved in the ether, whereas experiment has shown that this is not the case. Again, if the alcohol were present as the compound $C_6H_5\cdot CH_2\cdot O\cdot MgBr$, acetophenone should be present in the ethereal layer, which again is contrary to the experimental results; neither of the equations (10) or (11), therefore, can represent the facts of the case:

$$C_6H_5\cdot CH(OMgBr)\cdot CH_3 + C_6H_5\cdot CH(OH)_2 = C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot C(OH)(OMgBr)\cdot CH_3 \quad . \; . \; . \quad (10)$$

$$C_6H_5\cdot CH(OMgBr)\cdot CH_3 + C_6H_5\cdot CHO = C_6H_5\cdot CH_2(OMgBr) + C_6H_5\cdot CO\cdot CH_3 \quad . \; . \; . \quad (11)$$

The mechanism of the formation of the ortho-compounds is the only point which still requires elucidation. Although no direct experimental evidence in support of the present suggestion can be brought forward, there is, at any rate, some indirect evidence in its favour.

It is suggested that the first stage in the oxidation of benzaldehyde is the elimination of a molecule of water from two molecules of the hydrate of benzaldehyde. This may be effected by two different methods, either as in (12) or (13):

$$C_6H_5\cdot CH(OH)_2 + C_6H_5\cdot CH(OH)_2 = C_6H_5\cdot C(OH)_2\cdot CH(OH)\cdot C_6H_5 + H_2O \quad . \; . \; . \; . \quad (12)$$

$$C_6H_5\cdot CH(OH)_2 + C_6H_5\cdot CH(OH)_2 = C_6H_5\cdot CH(OH)\cdot O\cdot CH(OH)\cdot C_6H_5 + H_2O \quad . \; . \; . \; . \quad (13)$$

It is improbable that (12) represents the reaction, since benzoin would be almost certainly isolated, whilst Keane and Trantom have shown that no trace of this substance can be found. The loss of a second molecule of water is supposed to be the second step in the reaction, whereby hydroxydiphenylethylene oxide is produced:

$$C_6H_5\cdot CH(OH)\cdot O\cdot CH(OH)\cdot C_6H_5 = C_6H_5\cdot C(OH)\cdot CH\cdot C_6H_5 + H_2O \quad . \; . \; . \; . \quad (14)$$

(with the O bridging the C(OH) and CH carbons)

It may be noted that this substance is isomeric with two molecules of benzaldehyde, whilst it differs from the hypothetical

intermediate product suggested by Keane and Trantom, namely, $C_6H_5\cdot C(OH):C(OH)\cdot C_6H_5$.

Derivatives of ethylene oxide are known to undergo change with extreme ease (Tiffeneau, *Ann. Chim. Phys.*, 1907, [viii], **10**, 176, etc.), and the addition of a molecule of sodium hydroxide to this compound will result in the formation of the ortho-compound suggested by Keane and Trantom:

$$C_6H_5\cdot C(OH)\cdot CH\cdot C_6H_5 + NaOH =$$

$$C_6H_5\cdot C(ONa)(O\cdot C_7H_7)\cdot OH \quad . \quad . \quad . \quad (15)$$

A similar series of reactions will account for the formation of the ortho-derivative of acetophenone:

$$C_6H_5\cdot CH(OMgBr)\cdot CH_3 + C_6H_5\cdot CH(OH)_2 =$$
$$C_6H_5\cdot CH(CH_3)\cdot O\cdot CH(OH)\cdot C_6H_5 + Mg(OH)Br \quad . \quad . \quad . \quad (16)$$

$$C_6H_5\cdot CH(CH_3)\cdot O\cdot CH(OH)\cdot C_6H_5 =$$
$$C_6H_5\cdot C(CH_3)\cdot CH\cdot C_6H_5 + H_2O \quad . \quad . \quad . \quad (17)$$

$$C_6H_5\cdot C(CH_3)\cdot CH\cdot C_6H_5 + Mg(OH)Br =$$

$$C_6H_5\cdot C(OMgBr)(O\cdot C_7H_7)\cdot CH_3 \quad . \quad . \quad . \quad (18)$$

If a magnesium tertiary carbinyl haloid were employed in the place of a secondary compound, it is evident that no oxidation by an excess of the aldehyde would take place, since the formation of an intermediate ethylene oxide derivative would be impossible. This was put to the test by allowing benzaldehyde to react with magnesium diphenylmethylcarbinyl bromide, when no trace of an oxidation product could be found.

If the above explanation of the course of the reaction is correct, it is possible that a reaction may take place between a magnesium secondary carbinyl haloid and a ketone, for the formation of an ethylene oxide derivative from these substances is possible, according to the equation

$$C_6H_5\cdot CH(OMgBr)\cdot C_6H_5 + C_6H_5\cdot C(OH)_2\cdot CH_3 =$$
$$(C_6H_5)_2C{-}C(C_6H_5)\cdot CH_3 + H_2O + MgBr\cdot OH \quad . \quad . \quad . \quad (19)$$

If a compound of this constitution is formed, it will be impossible to foretell what will be the products of its hydrolysis, for the original substances may be reproduced, or benzophenone and phenylmethylcarbinol may be formed. Experiment showed that

combination of magnesium diphenylcarbinyl bromide with acetophenone actually occurred, whilst the products obtained from the reaction were diphenylcarbinyl ether and acetophenone.

Finally, experiments have been made to determine the nature of the action of ethyl acetate on magnesium carbinyl haloids, and it has been found that good yields of the acetates of the carbinols are produced. The reaction may be regarded as a case of double decomposition, and may be formulated:

$$C_6H_5\cdot CH(OMgBr)\cdot C_6H_5 + CH_3\cdot C(OH)_2\cdot OC_2H_5 = CH(C_6H_5)_2\cdot O\cdot C(OH)_2\cdot CH_3 + MgBr\cdot O\cdot C_2H_5 \quad . \quad . \quad . \quad (20)$$

It was shown in the earlier paper that formic ester reacts in such a manner with a magnesium carbinyl bromide as to yield, on hydrolysis, the bromide of the carbinol. This reaction may now be explained by assuming that the carbinyl formate is first formed as in (20), and is converted into the bromide by the action of magnesium ethoxybromide.

Further experiments in connexion with this subject are in progress, but it was thought desirable at this stage to correct the observations recorded in the former paper.

EXPERIMENTAL.

Action of Benzaldehyde on Magnesium Phenylbromide.

Several experiments were carried out in order to determine the conditions necessary for the production of tetraphenylethane. The yield of diphenylcarbinol produced by the reaction of equimolecular proportions of these substances was about 55 per cent. of the theoretical, and this was not affected by heating the Grignard product during several hours, or by alteration of the temperature at which the substances were allowed to react. In one experiment, however, 24 grams of magnesium (2 mols.) were allowed to react with an ethereal solution of 75 grams (1 mol.) of bromobenzene, and to the solution (still containing a large quantity of undissolved magnesium) was added a solution of 50 grams of benzaldehyde. The mixture was then poured into a mixture of ice and dilute hydrochloric acid. The chief product of this reaction was tetraphenylethane, of which 30 grams were obtained; the fraction containing benzhydrol could not be obtained in a crystalline condition.

Action of Benzophenone on Magnesium Phenyl Bromide.

This experiment was made in order to determine whether an excess of magnesium would lead to the formation of hexaphenylethane in a manner analogous to the formation of tetraphenyl-

ethane in the previous experiment. The only product of the reaction, however, was triphenylcarbinol, of which a 60 per cent. yield was obtained.

Action of Benzaldehyde on Magnesium p-*Tolyl Iodide.*

Two experiments were made, in one of which, (*a*), the amount of benzaldehyde was less than one molecular proportion, whilst in the second, (*b*), two molecular proportions of the aldehyde were added to the Grignard reagent. The chief product in (*a*) was phenyl-*p*-tolylcarbinol (m. p. 58°), whilst in (*b*) benzyl alcohol and phenyl-*p*-tolyl ketone were isolated. The latter substance solidified only when it was brought into contact with a specimen of the ketone obtained by Gattermann's method. It was recrystallised from alcohol, and melted at 60°. The oxime was prepared and analysed.

In these experiments, di-*p*-tolyl was formed in considerable quantity, and was best removed by pouring away the ethereal layer from the Grignard product before the decomposition of the latter with dilute acid.

Action of Benzaldehyde on Magnesium Methyl Iodide.

This reaction was carried out in the manner described in the former paper, but the products of the reaction were examined in more detail.

The fraction of the product boiling below 150°/15 mm. was kept over solid calcium chloride for some time to remove benzyl alcohol, and the remaining liquid was found to be pure acetophenone. This was obtained easily in a crystalline condition, and the oxime and the phenylhydrazone were prepared as confirmation of the nature of the substance.*

The fraction of the product boiling at 200—225°/15 mm. was recrystallised from alcohol, and the substance thus obtained melted at 53°. In order to separate from it a small quantity of impurity, it was dissolved in ether, and the solution was saturated with hydrogen chloride. The crystals which separated were recrystallised from alcohol (m. p. 112°), and were then allowed to remain in contact with a solution of sodium ethoxide.

The precipitated sodium chloride was removed, a little water was added to the clear filtrate, and, on keeping, crystals similar to the original substance were obtained, which, however, melted at 58°. These were compared with a specimen of phenyl styryl

* It has been found that in order to obtain phenylmethylcarbinol free from acetophenone, considerably less than the calculated quantity of benzaldehyde must be added to the solution of magnesium methyl iodide.

ketone prepared by condensing benzaldehyde with acetophenone in the presence of a solution of sodium hydroxide, and the two substances were found to be identical. Analyses of the hydrochloride and the dibromide (m. p. 169°) were published in the earlier paper. As a confirmatory test, the specimens were heated separately with phenylhydrazine, after which sufficient alcohol was added to each to produce a clear solution. The solutions, which were strongly fluorescent, deposited crystals melting at 135°, and a mixture of the two specimens had the same melting point. Each specimen gave the dark greenish-blue coloration when treated with nitrous acid which is characteristic of 1 : 3 : 5-triphenylpyrazoline, and the identity of the substance was established by an analysis.

The ethereal solution from which phenyl styryl ketone hydrochloride separated was distilled in a vacuum, and a fraction boiling at 220° was collected. This solidified on cooling, and it was partly soluble in dilute sodium hydroxide solution. The filtered alkaline solution was acidified, and the precipitate thus obtained was recrystallised from alcohol, when it melted at 80—81°. An alcoholic solution of the substance gave a reddish-violet coloration when a drop of a solution of ferric chloride was added to it. (Found: C = 80·1; H = 5·5. $C_{15}H_{12}O_2$ requires C = 80·3; H = 5·3 per cent.)

One gram of the substance was dissolved in a small quantity of alcohol, a small excess of an aqueous solution of hydroxylamine was added, and the mixture was boiled under a reflux condenser until no further precipitate was formed. The substance was separated and recrystallised from alcohol, from which solvent it was deposited in shining plates, melting at 141°. (Found; N = 5·99. $C_{15}H_{11}ON$ requires N = 6·3 per cent.)

The properties of the latter two substances and their analyses agree with those of dibenzoylmethane and 1 : 3-diphenyl*iso*oxazole respectively, and further confirmation of the identity of dibenzoylmethane was obtained by the preparation from it of monobromodibenzoylmethane (m. p. 92°) and of 1 : 3 : 5-triphenylpyrazole (m. p. 139°).

Action of Benzaldehyde on Magnesium Ethyl Iodide.

An ethereal solution of 79 grams (1½ mol.) of benzaldehyde was added to the well-cooled Grignard reagent obtained by the solution of 12 grams of magnesium in 78 grams of ethyl iodide, during which process the greyish, crystalline precipitate of magnesium phenylethylcarbinyl iodide, which first separated, was converted into a heavy, brown, viscous mass. The mixture was gently heated during twenty-four hours, the two layers were then poured

separately into cold dilute acid, and, after washing with dilute sodium carbonate solution, the two ethereal solutions were distilled. From the upper, ethereal layer, the only substance which could be separated was a small amount of benzaldehyde; this part of the reaction product did not contain benzyl alcohol. From the lower, viscous layer, two fractions were separated, namely, a colourless liquid, b. p. 90—155°/15 mm., weighing 86 grams (*A*), and a yellowish liquid, b. p. 160—240°, weighing 16 grams (*B*). From the distillate (*A*), 20 grams of benzaldehyde were separated in the form of the sodium hydrogen sulphite compound, whilst the residue distilled at 200—215° under the atmospheric pressure. This was oxidised by means of a dilute solution of potassium dichromate and sulphuric acid, when a further quantity of benzaldehyde (15 grams) was obtained, as well as 20 grams of pure phenyl ethyl ketone. There must have been present, therefore, in this fraction about 16 grams of benzyl alcohol and a mixture of phenylethylcarbinol and propiophenone.

Fraction (*B*), on keeping, became filled with a mass of crystals which, after being collected, washed with light petroleum, and recrystallised from hot alcohol, were obtained in colourless needles, melting at 84—85° (compare Abell, T., 1901, **79**, 929).

Dibenzoylethane is readily soluble in cold benzene, and is dissolved readily by boiling alcohol or light petroleum. It is not soluble in dilute sodium hydroxide solution, nor does an alcoholic solution of the substance produce any coloration when treated with ferric chloride. (Found: C = 81·10; H = 5·94. $C_{16}H_{14}O_2$ requires C = 80·7; H = 5·9 per cent.)

To a solution of 1·2 grams in alcohol, 0·8 gram of very finely powdered hydrazine sulphate was added, and, finally, 1 gram of sodium hydrogen carbonate. After the mixture had been kept overnight, water was added, and the precipitate was recrystallised from alcohol, in which it is not readily soluble. The compound melted at 223°, and agreed in its properties with 3 : 5-diphenyl-4-methylpyrazole (Abell, *loc. cit.*).

The combination of dibenzoylethane with phenylhydrazine is easily effected by warming equimolecular proportions of the two substances on the water-bath. The product separates from alcohol in colourless, silky needles, which melt at 125°:

0·1550 gave 15·5 c.c. N_2 at 16° and 742 mm. N = 9·26.
$C_{22}H_{18}N_2$ requires N = 9·03 per cent.

1 : 3 : 5-*Triphenyl-4-methylpyrazole* is readily soluble in carbon tetrachloride, and this solution does not react with a solution of bromine in the same solvent. The substance is soluble in concen-

trated mineral acids, but no action is observed when nitrous acid is added to the acid solutions of the compound.

3 : 5-*Diphenyl-4-methylisooxazole* is slowly precipitated when a solution of the diketone in dilute alcohol is boiled with a small excess of hydroxylamine hydrochloride. It forms shining plates, which melt at 127°:

0·235 gave 15·5 c.c. N_2 at 16° and 750 mm. N = 6·17.

$C_{16}H_{13}ON$ requires N = 6·0 per cent.

Bromodibenzoylethane is produced by allowing a solution of the ketone in carbon tetrachloride to react with a solution of the calculated quantity of bromine. The substance may be recrystallised from dilute alcohol, from which it separates in colourless prisms, melting at 65°:

0·1585 gave 0·0963 AgBr. Br = 25·70.

$C_{16}H_{13}O_2Br$ requires Br = 25·23 per cent.

Action of Benzaldehyde on Magnesium Propyl Iodide.

This reaction was carried out in the same manner as in the preceding experiment. Sixty-eight grams of propyl iodide were used, and the yellow fraction, which contained ethyldibenzoylmethane, weighed 23 grams. This fraction solidified on cooling, and, after purification by draining and recrystallisation from alcohol, dibenzoylpropane was obtained in long, colourless needles.

It melts at 87° (compare Auger, *Ann. Chim. Phys.*, 1891, [vi], **22**, 351), and is readily soluble in the common organic solvents. It is insoluble in water and in dilute alkali solutions, and its alcoholic solution is not coloured on the addition of a drop of a solution of ferric chloride. It is decomposed by sodium ethoxide in alcoholic solution into sodium benzoate and phenyl propyl ketone (semicarbazone, m. p. 187°). (Found: C = 81·16; H = 6·47. $C_{17}H_{16}O_2$ requires C = 81·0; H = 6·3 per cent.)

Bromodibenzoylpropane, $C_6H_5{\cdot}CO{\cdot}CBr(C_2H_5){\cdot}CO{\cdot}C_6H_5$, may be prepared in the usual manner. It separates from alcohol in hexagonal prisms, which melt at 52°.

Dibenzoylpropane reacts with hydroxylamine hydrochloride when the solutions are boiled for some hours. On adding a little water, 1 : 3-diphenyl-2-ethyl*iso*oxazole separates in long, colourless, silky needles, which melt at 93°. (Found: N = 5·3. Calc.: N = 5·6 per cent.) It is not altered by heating to the boiling point or by the action of phosphorus pentachloride.

Equivalent quantities of dibenzoylpropane and phenylhydrazine were heated on the water-bath during four hours, after which the

reaction mixture was distilled in a vacuum, when almost the whole of the substance passed over at 265°/15 mm. The distillate solidified on cooling, and was recrystallised from light petroleum.

1 : 3 : 5-*Triphenyl-4-ethylpyrazole* forms colourless needles, which melt at 84—85°:

0·1620 gave 15·4 c.c. N_2 at 17° and 750 mm. N = 8·85.

$C_{23}H_{20}N_2$ requires N = 8·6 per cent.

Action of Benzaldehyde on Magnesium iso*Propyl Iodide.*

This experiment was carried out in the usual manner, and a much greater proportion of unused benzaldehyde was recovered than in the preceding experiments. The chief product was a mixture of phenyl*iso*propylcarbinol and phenyl *iso*propyl ketone, only a very small amount of a substance with a higher boiling point than that of this mixture being obtained. From the fraction of higher boiling point was isolated less than 0·5 gram of a substance which crystallised from alcohol or light petroleum in bright yellow needles, melting at 110°. The quantity available was too small to admit of examination.

Action of Benzaldehyde on Magnesium Benzyl Bromide.

When magnesium is allowed to react with the calculated quantity of benzyl bromide dissolved in anhydrous ether, the proportion of magnesium which remains undissolved is much greater than in the experiments previously described. In some cases, the formation of 10 per cent. of dibenzyl was observed. Hence, in order to obtain pure phenylbenzylcarbinol by this method, it is necessary either to take considerably more benzyl bromide than is theoretically needed, or to diminish the amount of benzaldehyde to considerably less than one molecular proportion. Unless this precaution is adopted, the amount of phenyl benzyl ketone produced is so great as to render it almost impossible to obtain the carbinol in a pure condition. In the present experiment, the separation of these substances has not been attempted, since phenyldibenzoylmethane has a much higher boiling point than either deoxybenzoin or phenylbenzylcarbinol.

Dibenzoylphenylmethane is not readily soluble in hot alcohol, and is almost insoluble in the cold solvent. It separates from the solution in colourless needles, which melt at 149°:

0·1570 gave 0·4845 CO_2 and 0·0784 H_2O. C = 84·17; H = 5·56.

$C_{21}H_{16}O_2$ requires C = 84·00; H = 5·33 per cent.

The only reference to dibenzoylphenylmethane in the literature is in a paper by Japp and Lauder (T., 1896, **69**, 742), where a

substance, which melts at 119°, is described as having the composition required by this compound, although it does not react with phenylhydrazine.

The substance obtained in the present experiment reacts with phenylhydrazine when the two compounds are heated together on the water-bath during four hours. The product crystallises from alcohol, in which it is much more readily soluble than the original ketone, in needles, melting at 167°. An analysis showed that the substance was 1 : 3 : 4 : 5-tetraphenylpyrazole.

Bromodibenzoylphenylmethane is produced by mixing equivalent amounts of the ketone and bromine dissolved in carbon tetrachloride, and crystallises from alcohol in colourless prisms, melting at 147°.

Dibenzoylphenylmethaneoxime is obtained by boiling an alcoholic solution of the ketone with a small excess of free hydroxylamine during four hours. It crystallises from alcohol in fine needles, which melt at 153°:

0·2635 gave 13 c.c. N_2 at 15° and 750 mm. N = 4·61.

$C_{21}H_{17}O_2N$ requires N = 4·44 per cent.

The substance is soluble in dilute sodium hydroxide solution, and is reprecipitated on the addition of dilute acid. When heated above its melting point, or when an ethereal solution is mixed with phosphorus pentachloride, it loses a molecule of water, and is converted into 3 : 4 : 5-*triphenylisooxazole*, which is almost insoluble in alcohol and ether, and crystallises in needles, melting at 212°:

0·2359 gave 12 c.c. N_2 at 15° and 750 mm. N = 4·80.

$C_{21}H_{15}ON$ requires N = 4·72 per cent.

Action of Benzaldehyde on Magnesium Dimethylcarbinyl Iodide.

In the earlier paper, a substance, boiling at 165°/15 mm., of unknown constitution, was mentioned as constituting the chief product of this reaction. This substance has now been obtained in a crystalline condition, and proved to be styryl methyl ketone by analysis and by the preparation of the oxime (m. p. 116°) and of the phenylhydrazone (m. p. 156°). The latter substance may be easily converted into 1 : 5-diphenyl-3-methylpyrazoline by heating carefully to its boiling point. If the product is distilled in a vacuum, the distillate (boiling at about 250°) solidifies on cooling, and, after three recrystallisations from light petroleum, is obtained in colourless needles, which melt at 114°. Solutions of the pure substance in light petroleum or alcohol are not fluorescent. If a trace of sodium nitrite is added to the solution of the pyrazoline

derivative in hydrochloric acid, a vivid magenta coloration is produced. These two observations are contrary to those recorded in the literature, but have previously been made by Knorr (*Ber.*, 1893, **26**, 114).

Action of Acetaldehyde on Magnesium Phenylmethylcarbinyl Bromide.

A solution of magnesium phenyl bromide and acetaldehyde (4 mol.) was heated during twenty hours. After decomposing the reaction mixture with dilute acid, the ethereal extract was washed with a dilute solution of sodium hydroxide, and then distilled in a vacuum. The chief product was acetophenone, but a small quantity of a substance of higher boiling point was obtained, which was probably impure phenyl propenyl ketone. It reacted with phenylhydrazine to form a substance which was strongly fluorescent in solution, and of which an acid solution was coloured deep blue on the addition of nitrous acid; these properties are characteristic of 1 : 3-diphenyl-5-methylpyrazoline.

The solution of sodium hydroxide which had been employed to wash the ethereal extract of the reaction product was acidified with dilute acetic acid. A precipitate was obtained which, after filtration, was redissolved in alkali, and again precipitated with acid. The substance was then recrystallised from dilute alcohol, when it formed needles, melting at 59—60°. An alcoholic solution of the substance was coloured deep red by the addition of ferric chloride. An analysis showed that the substance was benzoyl acetone, and it was further characterised by the preparation from it of phenylmethyl*iso*oxazole, which forms shining plates, melting at 68—69°.

Action of Acetaldehyde on Magnesium iso*Propyl Iodide.*

This experiment was carried out in the usual manner, and the products which were isolated and identified were acetone and *iso*propyl alcohol. A small quantity of a yellow liquid, which boiled at 120—140°, was also obtained. This was soluble in water, and reacted violently with phenylhydrazine to form 1-phenyl-3 : 5-dimethylpyrazoline (Knorr, *Ber.*, 1887, **20**, 1105). The original liquid must therefore have been ethylideneacetone, but the quantity obtained was too minute to admit of complete purification and analysis.

Action of Benzaldehyde on Magnesium Diphenylmethylcarbinyl Bromide.

In an experiment in which benzaldehyde was allowed to react with the Grignard product obtained by the mixture of acetophenone with magnesium phenyl bromide, the only products which were isolated were diphenylmethylcarbinol and dibenzoylmethane. The latter substance was evidently produced by the action of the aldehyde on a small excess of acetophenone.

Action of Acetophenone on Magnesium Diphenylcarbinyl Bromide.

The grey, crystalline mass produced by the action of benzaldehyde on magnesium phenyl bromide was heated with one molecular proportion of acetophenone during twenty hours. There was no visible change in the character of the mass, but it was found that the acetophenone had combined in some manner with the magnesium compound, for only a trace of it was present in the upper layer at the end of the reaction. From the lower layer was obtained, on hydrolysis, a product containing nearly the whole of the acetophenone, and a substance which was found to be benzhydryl ether, m. p. 110°. (Found: C=89·35; H=6·41. $C_{26}H_{22}O$ requires C=89·14; H=6·28 per cent.)

Action of Ethyl Acetate on Magnesium Phenylmethylcarbinyl Iodide.

The Grignard product obtained by the addition of benzaldehyde to magnesium methyl iodide was mixed with one molecular proportion of pure ethyl acetate. The crystalline deposit immediately dissolved, a small quantity of heat being developed. After washing the ethereal solution with dilute acid, it was distilled under diminished pressure, and almost the whole of the product was a liquid boiling at 105—108°/15 mm. This liquid was found to be phenylmethylcarbinyl acetate, for it was hydrolysed by an alcoholic solution of potassium hydroxide, yielding acetic acid and phenylmethylcarbinol.

A similar result was obtained by the action of ethyl acetate on magnesium diphenylcarbinyl bromide, a good yield of the carbinyl acetate being produced.

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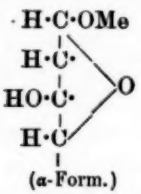
[*Received, Feb. 12th*, 1915.]

LX.—*Derivatives of a New Form of Glucose.*

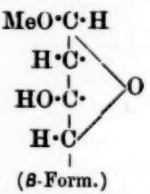
By James Colquhoun Irvine, Alexander Walker Fyfe (Carnegie Fellow), and Thomas Percival Hogg (Carnegie Scholar).

The recent account given by Fischer (*Ber.*, 1914, **47**, 1980) of the isolation of a third isomeric form of methylglucoside marks a new development in the chemistry of the sugars of great importance. An outline of the present position of the subject and its future possibilities has already been published (*Ann. Report*, 1914, 86), but, in making a further contribution to the problem, it is necessary to review the situation in some detail.

Until the past year, the opinion has prevailed that glucosides may be classified into two types, termed α- and β-forms respectively, which correspond with the two mutarotatory varieties of the parent sugar from which they are derived. According to this view, the isomerism exhibited by such glucosides is dependent on the configuration of the groups attached to a terminal carbon atom of the chain, and is unconnected with the internal linking of the sugar molecule. Taking the well-defined crystalline α- and β-methylglucosides as examples, this difference in structure, adopting the configurations indicated by recent researches, may be represented by the skeleton formulæ shown below, which show that each compound contains the same γ-oxidic linking:



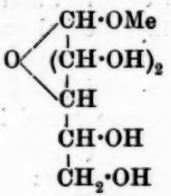
(α-Form.)



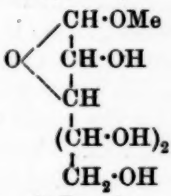
(β-Form.)

In practically every respect, the above formulæ may be regarded as satisfactory and consistent with the properties of the isomeric methylglucosides, their different solubilities, rotations, rates of hydrolysis, and their behaviour towards enzymes. Similar structures have also been applied to other artificial glucosides which have been isolated in two isomeric forms, and the same γ-oxidic linking has been shown to be present in several naturally occuring sugar derivatives, including salicin, sucrose, and maltose. The literature of the sugars certainly contains many other suggestions to account for the isomerism of glucosides, and the views expressed above were at first adopted with some hesitation, and only after a considerable amount of direct and collateral evidence had been

collected in their support has their acceptance become general. In a recent paper, however (Nef, *Annalen*, 1914, **403**, 204), arguments have been put forward in favour of the idea that the isomerism of α- and β-glucosides is due to a difference in the linking of the oxygen atom forming the internal ring in the sugar molecule. On this assumption, the formulæ suggested for α- and β-methylglucosides are:



(α-Form.)



(β-Form.)

Fischer has dealt so effectively with these ideas that it is unnecessary to produce any further argument to show that, whatever may be the cause of the isomerism of α- and β-methylglucosides, it is independent of the nature of the oxidic linking, which must be the same in each compound. It does not follow, of course, that all glucosidic compounds are derived from the γ-oxidic form of the parent sugar. Thus, the remarkable ease with which sucrose and other fructosides are hydrolysed indicates that these compounds are probably constituted on a different plan. As a result, the reasonable expectation has been held that, in addition to the fructosides, other hexosides would be discovered which, in constitution and properties, would differ from the standard forms represented by α- and β-methylglucosides. This expectation has been realised by Fischer, who obtained, from "glucose acetal," the new variety of methylglucoside, the instability of which towards hydrolysts closely resembles that of sucrose.

In the following communication, which shows that this methylglucoside is a mixture of isomeric hexosides derived from an entirely new variety of glucose, the expression "γ-methylglucoside" has been retained, but it should be understood that the name is provisional, and is used only to distinguish the substance from α- and β-methylglucosides. The index letter γ has thus no structural significance, either with regard to the configuration of the compound or to the coupling of the oxygen ring, and should not be confused with the expression "γ-oxidic linking."

At the date on which Fischer's paper on γ-methylglucoside was published, we had been engaged for some time on the investigation of derivatives of the new methylglucoside, and, in view of this collision of ideas, it is perhaps advisable to state the reasons which

led us into this line of work. With the object of synthesising glucosamine from glucose, a research was commenced in this laboratory in 1912 by one of us in collaboration with Mr. J. L. A. Macdonald, the first step of the proposed scheme being the preparation of trimethyl glucose in quantity. This involved a re-investigation of the preparation of glucosediacetone and of the general mechanism of the condensation of glucose with acetone. The reactions encountered were extremely complex, and it was evident that when glucose is treated with methyl alcohol and hydrogen chloride several products result, one being a form of methyl-glucoside much more reactive than the α- and β-varieties. This was shown by the result obtained when glucose acetal is extracted rapidly with a small quantity of acid acetone (a procedure which we imagined would yield glucosemonoacetone), as the product always contained a methylglucosidemonoacetone. A description of this product and of its dimethyl derivative has already been published (Macdonald, T., 1913, **103**, 1896), but it was subsequently recognised that the compound could not be derived from either α- or β-methylglucoside, as the latter compounds fail to react with acetone, and are, moreover, practically unaffected by heating at 40° with 0·25 per cent. hydrochloric acid. On the other hand, the methylglucosidemonoacetone referred to above was readily hydrolysed under these conditions, and was, moreover, characterised by its behaviour towards alkaline potassium permanganate solution, which it reduced instantaneously in the cold. Recognising that the properties of the parent methylhexoside must resemble those of a ketoside rather than those of an aldoside, we undertook its detailed examination, and were engaged on the problem when Fischer's paper on γ-methylglucoside appeared.

In addition to the properties recorded by Fischer, we find that γ-methylglucoside is characterised by (1) the remarkable ease with which it enters into condensation with acetone; (2) its capacity to reduce alkaline potassium permanganate solution, which is so striking as to suggest unsaturation; (3) its tendency to unite with one atomic proportion of oxygen to give a neutral product; and (4) the ready auto-condensation of this oxy-compound to give a product allied to the disaccharides. These properties, either individually or in combination, are practically unique in the sugar group, and introduced many serious complications into the methylation of the compound, a process which we adopted as likely to throw light on its constitution.

We find that γ-methylglucoside may be methylated by the silver oxide reaction in exactly the same manner as α- or β-methyl-glucoside, methyl alcohol being used as a solvent in the first and

second treatments with the alkylating mixture. Two subsequent methylations in methyl iodide solution sufficed to give tetramethyl γ-methylglucoside, which was purified by distillation in a high vacuum. The physical constants of this product are compared below with those of the fully methylated derivatives of α- and β-methylglucosides:

Tetramethyl α-methylglucoside.	Tetramethyl β-methylglucoside.	Tetramethyl γ-methylglucoside.
B. p. 108°/0·1 mm.	M. p. 40–41°.	B. p. 106°/0·25 mm.
$[\alpha]_D$ in water +147·4°	−17·3°	−14·6°
$[\alpha]_D$ in alcohol +153·9°	−17·4°	− 3·0°
n_D^{20} 1·4454	1·4450	1·4458
D_4^{20} 1·1082	—	D_4^{15} 1·1064

On first inspection, the above figures might lead to the conclusion that the new compound was merely a mixture of α- and β-tetramethyl methylglucosides. Such is not the case. The compound reduces alkaline permanganate instantaneously in the cold, and is hydrolysed by *N*/100-hydrochloric acid at 40°, conditions which do not affect the normal alkylated glucosides. The different behaviour of the three isomeric methylated glucosides on hydrolysis is illustrated in the following curves, which give clear evidence that tetramethyl γ-methylglucoside is a mixture of isomeric compounds.

In the case of the curve *BE*, the rise and fall in dextrorotation has been shown to be due to the hydrolysis of the α- and β-forms of tetramethyl methylglucoside at different speeds (Purdie and Irvine, T., 1904, **85**, 1049; see also Irvine and Cameron, T., 1904, **85**, 1071). The curve *CF* shows a similar rise and fall in lævorotation, from which it would appear that tetramethyl γ-methylglucoside (and consequently also the methylhexoside from which it is prepared) is similarly a mixture of two isomerides, one of which is more readily hydrolysed than the other. In this case, however, it is a dextro-form which is the less stable variety, whereas in the normal alkylated glucosides the reverse is the case.

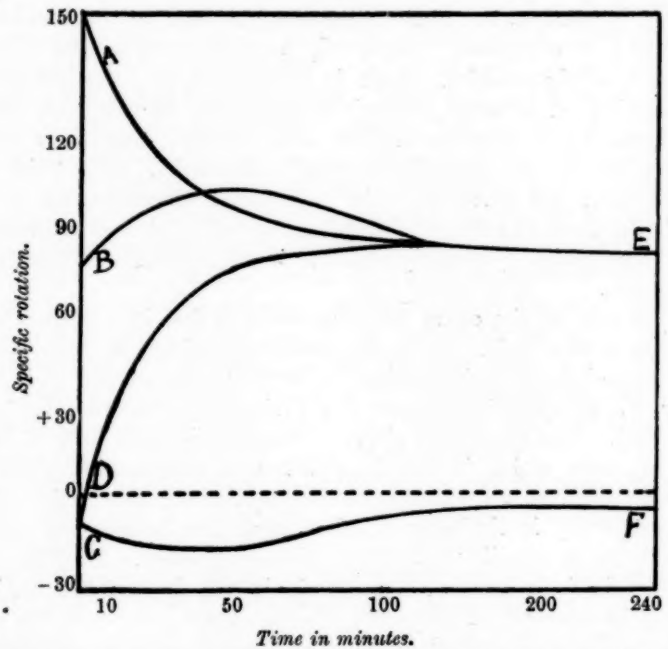
The product of hydrolysis is a tetramethylated hexose which, for want of a more appropriate name, may, in the meantime, be termed "tetramethyl γ-glucose." Unlike the characteristic crystalline tetramethyl glucose, the compound is a liquid, and is lævorotatory.

Comparison of the Tetramethyl Glucoses.

Tetramethyl α-glucose.		Equilibrium mixture of α- and β-tetramethyl glucoses.	Tetramethyl γ-glucose.
M. p. 89°		M. p. 75—80°	Liquid.
B. p. —		136°/0·8 mm.	122°/0·05 mm.
$[\alpha]_D$ in water +100·8°	→	83·3°	−3·8° → −7·2°
$[\alpha]_D$ in benzene +111·1°	→	88·9°	−17·1°
n_D		1·4588	1·4585

The new sugar retains the capacity to reduce alkaline potassium permanganate, which is characteristic of γ-methylglucoside, and is

FIG. 1.



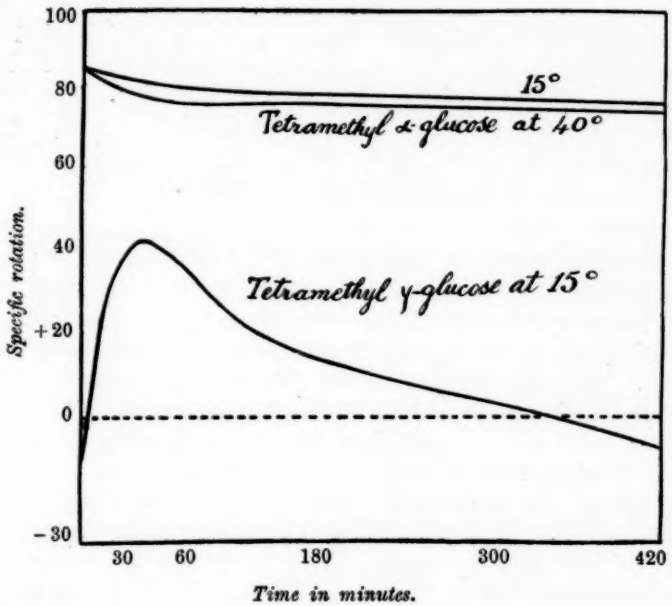
A E: Hydrolysis of tetramethyl α-methylglucoside at 100° with 2*N*-hydrochloric acid.
D E: ,, ,, β-methylglucoside ,, ,, ,,
B E: Hydrolysis of a mixture of α- and β-tetramethyl methylglucosides at 100° with 2*N*-hydrochloric acid.
C F: Hydrolysis of tetramethyl γ-methylglucoside at 100° with *N*/100-hydrochloric acid.

also distinguished from normal methylated glucoses in all its optical relationships. As, after distillation, it displays mutarotation, the compound presumably exists in two interconvertible forms, but the optical change observed thereafter on solution is

an increase in lævorotatory power. In the case of glucose, mono-, di-, and tetra-methyl glucose, the β-forms show, in solution, an increase in dextrorotation, and the equilibrium mixtures in each case are thus also dextrorotatory. Here the reverse holds true, and the only parallel which can be found in the substituted glucoses is furnished by trimethyl glucose (Irvine and Scott, T., 1913, **103**, 564), which displays the same optical irregularity.

Tetramethyl γ-glucose can be readily converted into the corresponding methylglucoside by the action at 15° of methyl alcohol containing 0·25 per cent. of hydrogen chloride. As an index of

FIG. 2.



the special reactivity of the sugar, it may be mentioned that the condensation takes place in a few minutes at this temperature, whereas, under parallel conditions, tetramethyl α-glucose requires twenty-four hours for complete reaction. During the formation of the alkylated γ-methylglucoside, the activity of the solution showed a double inversion (lævo → dextro → lævo), thus confirming the idea that the less stable form of the compound is dextrorotatory. The speed of this reaction, compared with that of the condensation of normal tetramethyl glucose under the same conditions, is best illustrated by the curve reproduced above.

It is evident that tetramethyl γ-glucose is a derivative of a much

more reactive form of glucose than the α- or β-variety, and the structure of the compound thus becomes an important question. The evidence available is, however, so far incomplete. The sugar reacts with phenylhydrazine and acetic acid, but is thereby resinified, and, in addition, a definite anilide or other crystalline derivative could not be obtained. On the other hand, the compound is readily reduced to give a tetramethyl hexitol, which is, presumably, tetramethyl sorbitol. The probable constitution of this compound and its bearing on the general problem will be referred to later. Again, when oxidised in the cold by the agency of alkaline potassium permanganate solution, tetramethyl γ-glucose gave rise to two distinct products. One of these was a neutral liquid, non-reducing and non-glucosidic, but nevertheless not a lactone or other recognisable derivative. It is possible that this substance is a pentitol ether or other degradation product of the sugar, and analysis certainly points to this conclusion. The second product was easily characterised, and consisted of a new form of tetramethyl gluconic acid, which was readily converted by heating in a vacuum into a tetramethyl gluconolactone.

Formation of Oxy-compounds from γ-Methylglucoside.

One of the most remarkable properties of γ-methylglucoside is the ease with which it condenses with acetone, the reaction taking place on gentle warming and in the absence of any recognisable catalyst. The essential product of this reaction appears to be a γ-methylglucosidemonoacetone. The isolation of this substance in the pure state has not yet been accomplished, and, in order to convert it into a volatile derivative, the compound was methylated by means of the silver oxide reaction, with an altogether unexpected result. On fractionation of the methylated products, the lower boiling portion proved to be a trimethyl oxy-γ-methylglucosidemonoacetone (b. p. 105—106°/0·025 mm.), whilst the portion of higher boiling point (200°/1·4 mm.) consisted of a condensation compound allied to the disaccharides, which may be termed provisionally anhydrobis(dimethyl oxy-γ-methylglucosidemonoacetone). The methylation process was therefore accompanied by oxidation of a new type, and the consequent formation of an additional hydroxyl group in the γ-methylglucoside residue. The product of this change then undergoes normal methylation, but a secondary reaction, consisting of the auto-condensation of two molecules with the loss of a molecule of water, takes place simultaneously. This is an important reaction, as it indicates the possibility of synthesising complexes allied to the disaccharides without the agency of acid catalysts.

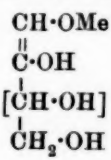
Constitution of the Compounds Described and of γ-Glucose.

Although the results now contributed throw a certain amount of light on the problem, further research will be necessary before definite conclusions as to the structure of γ-glucose and its derivatives can be drawn. Our deductions, therefore, cannot be regarded as final, and the structures suggested below are given with all reservation, and mainly with the object of rendering the scheme of reactions intelligible.

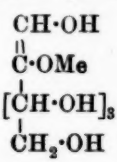
From the structural point of view, the most significant property common to all the derivatives of γ-glucose is the apparent unsaturation shown towards potassium permanganate. This at once suggests that the compounds may be allied to glucal, which, according to the most recent results (*Ber.*, 1914, **47**, 196), contains an ethylenic linking. No obvious modification of the glucal formula can, however, be found to accommodate the composition and reactions of the compounds under discussion without transferring the structures from the glucose to the fructose type. In the meantime, therefore, this possibility is passed over.

Obviously, the constitution of the form of glucose which gives rise to the new series of derivatives can be arrived at by determining the structure of γ-methylglucoside. Now, the results of methylation show that in the latter compound there are four unsubstituted hydroxyl groups, and, allowing for this factor and also for the behaviour towards potassium permanganate, the simplest possible formulæ fall into the three types shown below. In each case two stereoisomeric forms are possible.

Type A (Enolic).

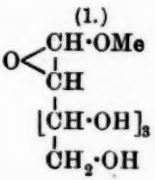


Type B (Enolic).

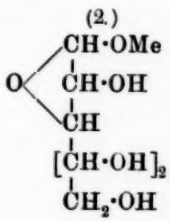


Type C (Oxidic).

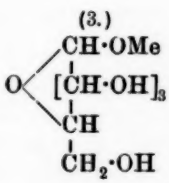
(1.)



(2.)

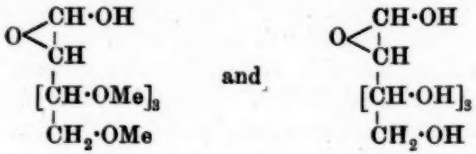


(3.)



For several reasons, the types A and B are unlikely, as probably substances of this nature would act, not as glucosides, but as reducing sugars. Further, the formation of such derivatives would imply that glucose can undergo the aldose $\rightleftharpoons$ enol $\rightleftharpoons$ ketose change in an acid system, and although this possibility cannot altogether be excluded (T., 1914, **105**, 1275), it is opposed to the results obtained by Lobry de Bruyn. At the same time, the unsaturated formulæ offer a ready explanation of the formation of oxymethylglucoside derivatives, but the bulk of the evidence is in favour of the formulæ C (1), C (2), or C (3). One possibility is omitted from the latter list, as the sugar obtained by hydrolysing tetramethyl γ-methylglucoside is not identical with γ-oxidic tetramethyl glucose.

Of the three alternatives to which the discussion is now limited, formula C (1) seems in best agreement with all the facts. By the adoption of this structure, tetramethyl γ-glucose and the parent γ-glucose would be represented, respectively, by the structures:



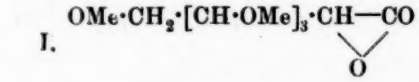
According to this view, the failure of tetramethyl γ-glucose to form a phenylosazone is explained, as the oxidation involved in osazone formation is due to the removal of hydrogen from the CH·OH group in the penultimate position in the sugar chain, or from a terminal $\cdot CH_2 \cdot OH$ group. Further, the optical properties of the hexitol formed from the sugar by reduction indicate that the compound contains two hydroxyl groups in spatial proximity. This was shown by the fact that the activity of the hexitol underwent a change of sign on the addition of boric acid, and, according to Böeseken (*Ber.*, 1913, **46**, 2612), this optical exaltation is only obtained when two hydroxyl groups are attached to neighbouring carbon atoms. This result, therefore, indicates that the tetramethyl hexitol may be represented by the formula

$$CH_2(OMe) \cdot CH(OMe) \cdot CH(OMe) \cdot CH(OMe) \cdot CH(OH) \cdot CH_2 \cdot OH,$$

which is consistent with the above structure for γ-glucose.

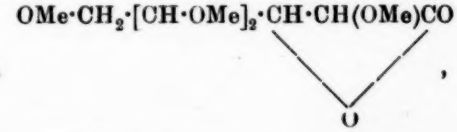
On the other hand, the fact that tetramethyl γ-glucose may be oxidised to give a definite unimolecular lactone is somewhat disconcerting, and is opposed to the evidence cited above.. The lactone is certainly different from that obtained from tetramethyl α-glucose, but is not a lactide or other bimolecular α-lactone, as it

shows a normal molecular weight. The two simplest structures for this lactone are:



I.

indicating that γ-glucose belongs to type C (1).



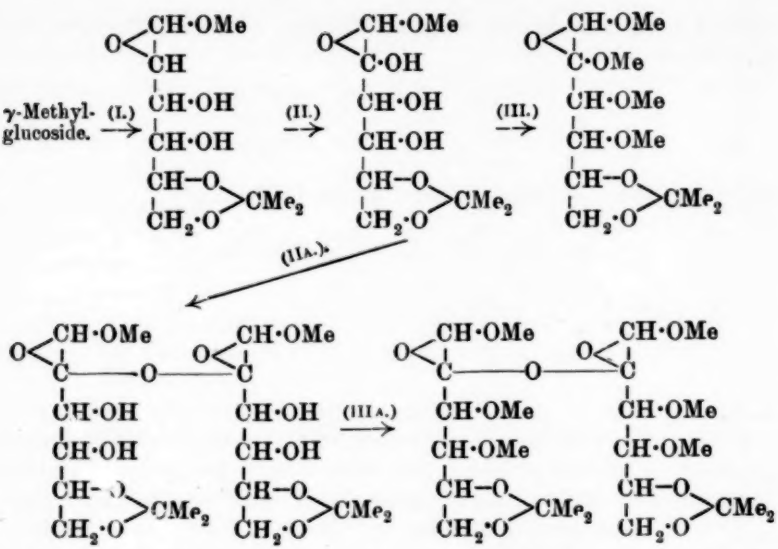
II.

indicating that γ-glucose belongs to type C (2).

It is difficult to determine which result is of greater value in the solution of this problem, the exaltation in the specific rotation of tetramethyl sorbitol in the presence of boric acid or the formation of a unimolecular lactone on oxidation. In the meantime, the question may be left open until further evidence regarding the application of Böeseken's methods to the sugar group is available, and, in the structural scheme subsequently given, a β-oxidic linking would apply equally well to explain the formation of all the compounds now described.

Structure of the Oxy-derivatives.

The addition of one oxygen atom to γ-methylglucoside, which takes place under the conditions described in the experimental part, introduces a new hydroxyl group into the molecule. Although this is a most unexpected result, there can be no reasonable doubt that this is the case, as, after methylation in the presence of acetone, a trimethyl oxy-γ-methylglucosidemonoacetone results. This compound is quite unique, as it is evidently derived from a reducing hexose containing six in place of five hydroxyl groups. Application of the provisional formula C (1) for γ-methylglucoside offers a feasible explanation for the formation of the oxy-compound, and also of the oxy-disaccharide derivative.



Stage I.: Condensation with Acetone.—No proof exists as to the location of the *iso*propylidene group, but the position provisionally selected appears to be the most probable one. Fructose forms a similar compound, which can be isolated by distillation.

Stage II.: Oxidation by Silver Oxide.—This product has not been isolated, as, under the conditions of the experiments, its existence is transitory.

Stage II.A: Auto-condensation.—The union of the hexose residues doubtless depends on the interaction of two tertiary hydroxyl groups, as, on the analogy of fructose, this group should be the most reactive part of the molecule.

Stages III. and III.A: Normal Methylation.

We are continuing the same line of investigation, and, in particular, hope to examine further the auto-condensation products of γ-methylglucoside and similar substances with a view to ascertaining if the synthesis of disaccharides can be accomplished through the agency of these compounds.

EXPERIMENTAL.

Methylation of γ-Methylglucoside.

The γ-methylglucoside used was prepared in essentially the manner described by Fischer, special care being taken to ensure that all the reagents used were free from acetone. This is a very necessary precaution. As the products of methylation are readily volatile, it was considered unnecessary to distil the glucoside, as

this process involves considerable loss. The compound was accordingly used in the form of a colourless syrup, which was practically devoid of action on Fehling's solution, and, when dried at 30°/15 mm., gave OMe=15·90. ($C_7H_{14}O_6$ requires OMe=15·98 per cent.)

Twelve grams of the glucoside were boiled under a condenser with 75 grams of methyl iodide, and, on the addition of 10 c.c. of pure methyl alcohol, a clear solution was obtained. To this, 55 grams of silver oxide were gradually added, and the alkylation was continued for eight hours, methyl alcohol being afterwards used as the extracting agent. The syrupy product, isolated as usual, was subjected to a second methylation, in which the same proportions of the alkylating mixture were employed, and, in this case also, a small quantity of methyl alcohol was necessary to obtain complete solution. After this treatment, the product was freely soluble in methyl iodide, and in the third methylation, in which 30 grams of oxide and 45 grams of iodide were employed, no extraneous solvent was necessary. The methylated glucoside was extracted with ether and isolated by distillation at the Gaede pump. In this way, 7 grams of a colourless, mobile liquid were obtained, whilst a viscous residue (1·4 grams) remained undistilled. The boiling point of the distilled product was, however, indefinite, and, in addition, the refractive index (n_D 1·4475) and methoxyl content (OMe=58·1 per cent.) showed that the methylation was still incomplete. The methylated glucoside was accordingly subjected to a fourth alkylation by solution in 45 grams of methyl iodide and treatment with 30 grams of silver oxide. On distillation of the resulting syrup, 6·3 grams of tetramethyl γ-methylglucoside were collected at 115—116°/0·5 mm., and from this specimen, on further fractionation, the pure compound was obtained (b. p. 106°/0·25 mm.).

Found: C=52·42; H=8·79; OMe=61·1.

$C_{11}H_{22}O_6$ requires C=52·80; H=8·80; OMe=62·0 per cent.

It was evident that small quantities of other products possessing a lower carbon content were also produced in the reaction, judging from analyses conducted on fractions of both lower and higher boiling point than the main fraction referred to above. For this reason, the re-fractionation of tetramethyl γ-methylglucoside must be carried out with great care, and, in our experience, it is better to control the progress of the distillation by determination of the refractive index rather than by variations in the boiling point, as little trust can be placed in the latter factor in fractionations under highly diminished pressure.

Tetramethyl γ-methylglucoside is a colourless, mobile liquid

readily soluble in water and in organic solvents. The compound is non-reducing, but is hydrolysed by very dilute acids with extreme ease. The most striking property of the compound is its capacity to reduce alkaline potassium permanganate solution in the cold. The following constants were determined:

n_D 1·4458, D_4^{15} 1·1064, M_D 60·23 (Calc. 60·65).

Solvent.	*c.*	$[\alpha]_D^{20}$.
Water	2·4995	−14·6°
Alcohol	2·4985	− 3·0
Acetone	2·6215	− 5·5
Benzene	2·6665	− 4·3

The above values are initial specific rotations determined without delay. In the case of the aqueous and the benzene solutions, no change in activity was observed on keeping, but the acetone and the alcoholic solutions showed considerable variation, the former increasing in fifteen hours to $[\alpha]_D$ −7·6°, and the latter to −11·8°. These alterations are doubtless due either to oxidation or to reaction with the solvent.

Hydrolysis of Tetramethyl γ-Methylglucoside. Tetramethyl γ-Glucose.

A 5 per cent. solution of the alkylated glucoside in *N*/100-hydrochloric acid showed an increase in specific rotation when preserved at 40°, but, as the hydrolysis at this temperature was slow, the solution was thereafter heated at 100°. The specific rotation increased to a maximum and then diminished to practically the initial value, some of the figures indicating this rise and fall being reproduced below, the value being calculated on the concentration of glucoside originally present:

Initial specific rotation :—	− 9·2°
After 30 minutes at 40°.....	−12·5
„ 30 „ „ 100°	−17·5
„ 60 „ „ 100°.....	−10·0
„ 90 „ „ 100°.....	− 8·2 (constant).

At this stage, although the hydrolysis was apparently complete, the acid concentration was raised to *N*/10 and the heating continued at 100° for forty-five minutes, during which time the specific rotation diminished to the constant value −5·4°. On removal of the acid with silver carbonate, and evaporation of the solvent under diminished pressure, a clear syrup remained. This was dissolved in ether, and the solution was dried over magnesium sulphate and evaporated. The residue consisted of tetramethyl γ-glucose in the form of a clear, viscous syrup, which was purified by distillation (b. p. 122°/0·05 mm.).

In subsequent preparations of the sugar, the hydrolysis of the glucoside was carried out from start to finish with *N*/10-acid at

100°. Although under these conditions the reaction is complete in sixty minutes, it is somewhat difficult to determine the end-point polarimetrically, as, with the higher concentration of acid, the rise and fall of rotation is obliterated, so that the optical value remains practically steady.

Tetramethyl γ-glucose is a colourless liquid resembling glycerol in appearance. The compound possesses solubilities similar to those of the glucoside from which it is derived, reduces Fehling's solution actively on warming, and also alkaline potassium permanganate in the cold.

Found: C = 50·65; H = 8·47; OMe = 50·6.

$C_{10}H_{20}O_6$ requires C = 50·85; H = 8·47; OMe = 52·5 per cent.

Owing to the viscosity of the liquid and the small quantity of material available, the following density determination may be regarded as only approximate:

D_4^{15} 1·1644, n_D 1·4585, M_D 55·36 (calc. 56·03).

Before determining the specific rotations, the sugar was redistilled, so as to increase the proportion of one of the possible mutarotatory forms. Mutarotation was, however, only detected in the case of the aqueous solution.

Solvent.	*c.*	$[\alpha]_D^{20}$.
Water	2·080	− 3·85° ⟶ −7·21
Methyl alcohol	1·827	−19·7
Benzene	1·641	−17·1

Reactions of Tetramethyl γ-Glucose.

In practically every respect the reactions of the new form of tetramethyl glucose are abnormal. Its behaviour towards alkaline permanganate and its optical irregularity have already been referred to, and are opposed to all precedent in compounds possessing the glucose configuration.

Action of Phenylhydrazine.—An aqueous solution of the sugar when heated in boiling water with phenylhydrazine and acetic acid reacted very readily. Gas was evolved, and a dark-coloured oil separated. Attempts to purify this compound failed, but, from its solubilities and reactions, we are inclined to the opinion that it is of the nature of a hydrazone, and not an osazone.

Action of Aniline.—The anilides of alkylated sugars are usually well defined and crystalline, but, although the standard conditions (Irvine and M'Nicoll, T., 1910, **97**, 1449) were followed in the case of tetramethyl γ-glucose, the sugar was recovered unaltered from the reaction.

Condensation with Methyl Alcohol.—A 1 per cent. solution of the sugar in methyl alcohol containing 0·25 per cent. of hydrogen chloride showed immediate and extensive alterations in rotatory

power, indicating that condensation proceeded rapidly at the temperature of the room. The rotation altered from lævo to dextro, and then underwent a second inversion from dextro to lævo, the reducing action on Fehling's solution meanwhile disappearing. Some of the optical observations which are embodied in the curve reproduced in the introduction are given below, together with the similar changes in rotation shown during the condensation of tetramethyl α-glucose with methyl alcohol under the same conditions and at 40°. In each case the specific rotations are calculated on the concentration of the sugar originally present.

Solvent: Methyl Alcohol containing 0·25 *per cent. of Hydrogen Chloride.*

Time from first reading.	Tetramethyl γ-glucose.	Tetramethyl α-glucose.	
	T=15°.	T=15°.	T=40°.
0 minutes.	−10·4°	+85	+84
2 ,,	7·5	—	—
3 ,,	3·8	—	—
5 ,,	+3·8	—	—
13 ,,	24·6	—	—
40 ,,	43·2	81	79·1
85 ,,	32·0	—	—
200 ,,	12·0	—	—
260 ,,	6·6	78	76·5
Constant	−22·5	(incomplete in 30 days)	75·1

The tetramethyl γ-methylglucoside isolated from the above experiment showed n_D 1·4470.

Oxidation with Potassium Permanganate.—A solution of 2 grams of the sugar in 200 c.c. of water was rendered alkaline by the addition of 16 c.c. of 2*N*-sodium hydroxide, and thereafter 56 c.c. of potassium permanganate solution (1 c.c. = 0·01575 gram $KMnO_4$) were gradually added, with frequent shaking. Carbon dioxide was then bubbled through the liquid, which was filtered, and evaporated to dryness under diminished pressure. The solid residue was extracted with boiling ether, and the solution was dried and evaporated, a colourless, mobile liquid (0·6 gram) being thus obtained. As this quantity of material did not permit of further purification, we are unable to identify the product, but the following facts regarding it may be stated. The compound is neutral, and practically devoid of action on Fehling's solution at the boiling point. It still reduces alkaline permanganate, but is neither a lactone nor an ester, and contains 55·2 per cent. of methoxyl. As stated in the introduction, these results indicate that the compound is possibly a tetramethyl pentitol.

The main oxidation product remained in the solid residue, referred to above, in the form of a potassium salt, and was isolated by acidification with hydrochloric acid and extraction with ether

in Hagemann's apparatus. After drying the ethereal solution and evaporation of the solvent, an acid syrup remained, which weighed 1·4 grams. This was dried until constant in weight at 60°/1 mm. Analysis and titration showed the compound to be a *tetramethyl-gluconolactone* (n_D 1·4519).

Found: C=51·03; H=7·66.

$C_{10}H_{18}O_6$ requires C=51·28; H=7·69 per cent.

The molecular weight, determined in benzene by the freezing-point method, was 228. (Calculated for a unimolecular lactone, 234.) The behaviour of the compound on titration was characteristic of a lactone.

0·1200 Dissolved in dilute alcohol was titrated with sodium hydroxide solution (1 c.c.=0·00411). Found: (1) by direct titration in the cold, that 5·00 c.c. alkali were required, and (2) after heating with excess of alkali and titration to the neutral point with acid, that 5·13 c.c. alkali were used. $C_{10}H_{18}O_6$ requires 5·00 c.c.

The lactone differs widely in rotation from all the other compounds now described. Solvent: ethyl alcohol, $c=1$, $[\alpha]_D$ +59·4°. A solution in aqueous alcohol showed the usual diminution in rotatory power, which is a common property of lactones allied to the sugars.

Initial $[\alpha]_D$ +59° ⟶ +46° in four hours.

Reduction of Tetramethyl γ-Glucose.—This reaction was carried out in practically the same manner as already described for the reduction of tetramethyl mannose (Irvine and Paterson, T., 1914, **105**, 898), except that the ethereal solution of the sugar was very dilute, and only 2·5 per cent. sodium amalgam was used. After two successive reductions, the product, isolated by vacuum distillation (b. p. 125°/0·4), proved to be a *tetramethyl sorbitol.*

Found: C=50·57; H=9·19; OMe=51·5.

$C_{10}H_{22}O_6$ requires C=50·42; H=9·25; OMe=52·1 per cent.

n_D 1·4568, $[\alpha]_D$ in water −6·2° (c=1·463).

The above specific rotation was permanent, but a solution of the compound in $N/2$-boric acid showed curious optical changes, indicating that interaction of the solutes took place.

Time from the addition of boric acid.	Specific rotation.
10 minutes	−15·0°
25 ,,	8·2
35 ,,	inactive
50 ,,	+6·8
300 ,,	−2·7 (constant).

The significance of this result is discussed in the introduction.

Condensation of γ-Methylglucoside with Acetone.

On heating γ-methylglucoside with pure acetone under a condenser, the compound passes into solution, owing to condensation with the solvent. On alkylating a solution obtained from 12 grams of the glucoside, in the manner described above, by the addition of methyl iodide (6 mols.) and silver oxide (3 mols.), simultaneous oxidation and methylation took place. Acetone was used as the extracting agent, and the syrup left on evaporation of the solvent was freely soluble in methyl iodide. No extraneous solvent was thus required for the second methylation, in which the same proportions of oxide and iodide were used.

On distilling the product under 0·05 mm. pressure, 7·9 grams of a colourless distillate were obtained between 115° and 122°, whilst 4 grams of a viscous syrup remained undistilled. Two distinct products were evidently present, and these were separately re-methylated and re-fractionated until pure. The compound of lower boiling point (105—106°/0·025 mm.) proved to be *trimethyl oxy-γ-methylglucosidemonoacetone.*

Found: C = 53·63; H = 8·41; OMe = 41·3.

$C_{13}H_{24}O_7$ requires C = 53·42; H = 8·21; OMe = 42·4 per cent.

n_D 1·4493, D_4^{15} 1·1133, M_D 69·33 (calc. 70·37).

The divergence of the molecular refraction from the calculated value is not great, and may be accounted for by the uncertainty as to which constants should be included in the calculation. Greater trust is placed in the analytical figures, which are so far removed from those required for a fully methylated glucoside that there is no possibility of such a compound being present. The specimen described above contained, however, at least two isomeric compounds, as, on distilling the liquid in two equal fractions, the following results were obtained:

n_D of liquid distilled = 1·4500.

	B. p.	Pressure.	n_D	OMe
Fraction I.	110–113°	0·05 mm.	1·4493	40·7
Fraction II.	105–106°	0·025 mm.	1·4491	41·3 per cent.

Despite the apparent identity of the two fractions and the constancy of refractive index and analytical composition, they differed in rotatory power as shown below ($c = 2·5$):

	Acetone.	Ethyl alcohol.	Benzene.	Methyl alcohol.
Fraction I.	—	—	—	−3·4°
Fraction II.	+7·6°	+5·3°	+3·2°	inactive

Hydrolysis.—On heating a 5 per cent. solution of trimethyl oxy-γ-methylglucosidemonoacetone in *N*/10-hydrochloric acid

at 90°, the rotation altered from lævo to dextro, and in fifty minutes attained the constant value $[\alpha]_D$ +41°. At this stage, only the *iso*propylidene residue had been removed, as the liquid was without action on Fehling's solution, and the product, isolated in the usual manner, had the composition of a *trimethyl oxy-γ-methylglucoside.*

Found: OMe = 48·7.

$C_{10}H_{20}O_7$ requires OMe = 49·2 per cent.

Prolonged heating under the same conditions removed the glucosidic group, but the products of the change were not further examined.

Examination of the Distillate of High Boiling Point.—The second product of higher boiling point, obtained in the simultaneous alkylation and oxidation of γ-methylglucoside in the presence of acetone, was methylated five times and fractionated. It consisted of a very viscous, clear syrup boiling at 200°/1·4 mm., and was readily soluble in organic solvents.

Found: C = 53·57; H = 8·12; OMe = 37·5, 37·1.

$C_{24}H_{42}O_{13}$ requires C = 53·53; H = 7·81; OMe = 34·6 per cent.

Although the analytical figures are doubtless affected by the presence of higher methylated products, they point to the substance being *anhydrobisdimethyl oxy-γ-methylglucosidemonoacetone.* The relationship of the compound to a disaccharide is also indicated by the viscosity, high boiling point, refractive index (n_D 1·4587), and the value of the molecular weight.

Found: In alcoholic solution by the ebullioscopic method, M.W. = 532; in benzene solution by the cryoscopic method, M.W. = 366.

$C_{24}H_{42}O_{13}$ requires M.W. = 538.

One molecular-weight determination thus gave an abnormal result, which we are unable to explain, but the same irregularity was encountered on a former occasion in the case of octamethyl diglucose, and the bulk of the evidence shows that the compound described above is not a derivative of a hexose, but of a disaccharide.

Part of the expense of the investigation was defrayed by a research grant received from the Carnegie Trust, for which we wish to express our indebtedness.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received March 6th*, 1915].

ANNUAL GENERAL MEETING,

MARCH 25TH, 1915.

Professor W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

Messrs. F. G. POPE and G. F. MORRELL were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society for the past year was presented by the President, and taken as read, and a statement as to the income and expenditure for 1914 was made by the Treasurer. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31st, 1914, was proposed by Mr. JOHN SPILLER, seconded by Dr. R. H. PICKARD, and carried unanimously.

A vote of thanks to the Auditors for their services, proposed by the TREASURER, was seconded by Dr. F. L. PYMAN, and acknowledged by Sir JAMES J. DOBBIE.

REPORT OF COUNCIL, 1914—1915.

ON December 31st, 1913, the number of Fellows was 3,201; 138 Fellows were elected in 1914, and 5 were reinstated, making a gross total of 3,344. The Society regrets the loss of 27 Fellows by death; 46 Fellows have resigned, the elections of 7 Fellows have become void, and 59 Fellows have been removed for non-payment of annual subscriptions.

The total number of Fellows, therefore, on December 31st, 1914, was 3,205, showing an increase of four over that of the preceding year. This falling-off in the rate of increase of membership is due to a decrease of 26 in the number of elections, which were 164 in 1913, and to an increase of 19 in the number of those who have ceased to be Fellows.

The Council desires to record that the following 3 Fellows have been killed in action:

Cecil Reginald Crymble (1911).
John Gunning Moore Dunlop (1909).
Charles Cochrane Iles (1914).

The names of the deceased Fellows, with date of election, are:

Daniel Bain (1884).
Frank Baker (1907).
Joseph Bemrose (1879).
Henry Boyers (1901).
Jeffrey Hale Burland (1884).
Harry Burrows (1902).
Charles Cunningham Connor (1875).
Cecil Reginald Crymble (1911).
Arthur Ellson Davies (1866).
Robert Kennedy Duncan (1906).
John Gunning Moore Dunlop (1909).
Henry Fairrie (1895).
Harry Marshall Freear (1885).
John Gibson (1892).
Christopher Clarke Hutchinson (1884).
Charles Cochrane Iles (1914).
John Esson McGillvray (1909).
Theodore Maxwell (1865).
Frederick George Richards (1905).
Edward Riley (1851).
Maung San U (1908).
John Smyth (1873).
William Frederick Keating Stock (1866).
Sir Joseph Wilson Swan (1875).
Joseph William Thomas (1875).
Francis Vacher (1882).
Robert Williamson (1874).

The following Fellows have resigned:

John Bateman.
Robert Gordon Bibby.
John Frank Blackshaw.
Richard Bodmer.
Arthur Forbes Braid.
Charles Edward Browne.
Percy Charles Burr.
Arthur Colefax.
Bernard Collitt.
Arthur William Cooke.
Samuel Irwin Crookes.
Gilbert Howard Daniel.
William Henry Dickinson.
Edric Druce.
Archibald Sefton Elford.
Frank Evershed.
Sir Frederick William Fison, Bart.
Robert Cecil Gale.
Thomas Girtin.
Thomas Sidney Haines.
Archibald Hall.
William Mogford Hamlet.
Arthur Stanley Hemmy.
Carl Richard Hennings.
Harold Hibbert.
Eric John Holmyard.
Henry Williams Jones.
Arthur Robert Laws.
Ernyst Graham Laws.
Charles Herbert Bell Longman.
Aylmer Henry Maude.
Frederick Morton.
Wilfrid Roberts Powell.
Kali Prosonuo Rai.
Walter Ramshaw.

Thomas Anderson Reid.
Willie Macro Seaber.
William Bush Schober.
Herbert Stephen Shorthouse.
John Kirby Shrimpton.
William Veysey Smith.
Frederick William Steel.
Robert Hawks Walton.
Percy George Ward.
William John Wilson.
Stuart Jardine Norris Wolfenden.

The number of Honorary and Foreign Members at the end of 1913 was 35, but since then the Society has had to record the loss of:

Johann Wilhelm Hittorf.
Adolph Lieben.
Carl Liebermann.

The total number of Honorary and Foreign Members, therefore, at the end of 1914 was 32. It is hoped that obituary notices of these deceased Honorary and Foreign Members will be published during the coming year.

The Council are very gratified to report that a considerable number of the Fellows are serving with His Majesty's Forces. It has been decided that, in such cases, the action of Bye-law IV. with regard to the removal of Fellows for non-payment of annual subscriptions shall be suspended until after the termination of the war.

The hearty congratulations of the Council are offered to the following Fellows, who have reached their Jubilee:

George Ward, elected April 21st, 1864.
George Walter Knox, elected June 16th, 1864.
Charles Estcourt, elected February 2nd, 1865.
Thomas Porter Blunt, elected February 2nd, 1865.

Fellows resident abroad have been notified that owing to the possible risk in transmission caused by the war, the publications of the Society will be sent only to those who have given the necessary authorisation to the Assistant Secretary.

During the year, 310 scientific communications were made to the Society; 235 of these have been published already in the Transactions, and abstracts of all but two have appeared in the Proceedings.

The volume of Transactions for 1914 contains 2,909 pages, of which 2,830 are occupied by 272 memoirs, the remaining 79 pages being devoted to the Obituary Notices, the Faraday Lecture, the Report of the International Committee on Atomic Weights, the

Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contained 238 memoirs occupying 2,173 pages. The Journal for 1914 also contains 4,757 abstracts, which extend to 2,068 pages, whilst the abstracts for 1913 numbered 5,978 and occupied 2,520. This diminution is due partly to the decrease in the number of papers published in the journals which have been available for abstraction, and partly to the failure to obtain many of the Continental journals since the commencement of the war. It is hoped that before long copies of these journals will be obtained and abstracted.

In the earlier part of the year the abstracts had shown the usual increase of numbers in comparison with the corresponding period in the preceding year.

The Abstracts may be classified as follows:

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry		1,543
Physiological Chemistry		592
Chemistry of Vegetable Physiology and Agriculture		336
	1,212	2,471

PART II.

General and Physical Chemistry		1,044
Inorganic Chemistry		451
Mineralogical Chemistry		109
Analytical Chemistry		682
	856	2,286
Total in Parts I. and II.	2,068	4,757

In accordance with a decision of the Council, the issue of the Proceedings as a separate publication ceased with the completion of the thirtieth volume at the end of 1914; the Proceedings are now published monthly in an abbreviated form with the Journal. Summaries of papers are no longer published in the Proceedings, but papers published in the Journal are now dealt with in the Society's Abstracts, so that the latter are rendered more complete than formerly. The Council have under consideration a scheme which will provide for the occasional delivery of lectures on special subjects; it is hoped that these will provide a useful addition to

the matter contained in the Annual Reports, which are necessarily of a more general character.

The Transactions for 1914 contain obituary notices of Matthew Algernon Adams, Joseph Carter Bell, William Popplewell Bloxam, Harry Burrows, James Tudor Cundall, Robert Kennedy Duncan, John Gibson, Sir Walter Noel Hartley, John Heron, Julius Lewkowitsch, Hugh Marshall, and George Matthey. The Council wish to express their indebtedness to the Fellows who wrote the notices, and to those Fellows who have contributed to Volume XI. of the Annual Reports.

The Faraday Lecture, entitled "Electrolytic Dissociation," was delivered by Dr. Svante Arrhenius on May 25th, 1914, and appears in the Transactions, Volume 105, p. 1414. The lecture, as on all previous occasions, was given in the theatre of the Royal Institution, the use of which was kindly granted by the Managers.

In the last Report of Council it was stated that the question of re-issuing Volume I. of the Memorial Lectures was under consideration, and that a circular had been sent out inviting Fellows who wished to purchase this volume to notify the Assistant Secretary. The number of applications received for this volume is not such as to warrant the Council in reprinting it at present.

The Longstaff Medal for 1915 has been awarded to Dr. M. O. Forster, F.R.S., and the presentation will be made at the Annual General Meeting on March 25th.

The congratulations of the Society have been conveyed to Professor A. P. N. Franchimont on his completing forty years as Professor of Organic Chemistry in the University of Leyden; also to the Reale Accademia delle Scienze, Turin, on the celebrations of the centenary of Ascanio Sobrero.

In common with other learned Societies in Great Britain, the Council unanimously passed the following resolution:

"That the President and Council of the Chemical Society, at their first meeting of the Session, desire to be associated with the statements and opinions set forth by certain scholars and public men in their manifesto published in *The Times* of October 21st, 1914."

This resolution was communicated to the Press.

During the past year the question of uniformity in bibliographical abbreviation has been considered by a committee of the International Association of Chemical Societies. In response to a request made by this committee, the Council have decided that the Chemical Society should adopt the scheme of abbreviations which will be drawn up for universal use, but owing to the war the work of the International Association has been interrupted.

Sir William Ramsay, Professor Percy F. Frankland, and Professor Arthur W. Crossley were nominated to represent the Society at the meetings of the Association.

Since the last Anniversary Meeting, three Informal Meetings have been held, on April 30th, October 22nd, 1914, and on January 14th, 1915. These meetings were instituted to afford Fellows opportunities of meeting the Officers and Council as well as one another; it is satisfactory to record that they have been attended with increasing success.

During the past year the Society has received gifts of plaster busts of Berzelius and Liebig from the Right Honourable Sir Henry E. Roscoe, and of a medal in commemoration of Scheele from Professor Kirkaldy. The cordial thanks of the Council have been conveyed to these donors. The busts have been placed in the Council Room, and the medal added to the collection in the Library.

Professor J. Millar Thomson accepted the invitation of the Council to act as the Society's representative on the British Organising Committee of the International Congress of Photography, 1915, whilst Mr. J. J. Beringer represented the Society at the Centenary Celebration of the Royal Geological Society of Cornwall.

Professor H. E. Armstrong has consented to act for five years as the Society's representative on the Committee of the Lawes Agricultural Trust.

It has been decided that the Anniversary Dinner shall not be held this year.

The attention of Fellows has been called to the regulations governing the Hadfield Research Prize of the value of £200 which will be awarded by the Council of the Iron and Steel Institute in May, 1916, for original research on the "Different Forms or Combinations of Carbon in Iron, Steel, and Alloys of Iron with other Elements." This sum will be awarded for the best report presented before February 1st, 1916.

An announcement was made (see Proc., p. 155) that a Fund has been established in connexion with the van't Hoff Memorial for the endowment of research in pure and applied chemistry. The amount available during 1915 for this purpose is about £67.

A further contribution of £10 has been made in support of the work carried on by the International Commission in preparing the next volume of the International Tables of Constants and Numerical Data. In response to a wish expressed by the Commission, the Council appointed a Committee to criticise the form and arrangement of the Tables; the report drawn up by the Committee has

been forwarded to the Commission and has received their careful consideration.

The Council have decided that books may be borrowed from the Reference Library under the following conditions:

"Fellows are permitted to borrow books from the Reference Library either for one night, or from Saturday to Monday. Such volumes must be applied for personally at the usual time of closing the Library, and an undertaking must be signed that the volumes will be returned not later than one hour after the reopening of the Library on the following morning. The privilege does not extend to volumes of special value or rarity, and will not be continued to any Fellow who does not strictly comply with these conditions."

Since Fellows were not aware that some of the more important journals could be borrowed, a list of those available was inserted as a loose leaflet in the Journal for April.

The additions to the Library comprise 95 books, of which 41 were presented, 265 volumes of periodicals (representing 243 Journals), and 45 pamphlets, as against 137 books, 510 volumes of periodicals (representing 241 Journals), and 86 pamphlets last year.

In a year when so many unexpected events have occurred, it is not surprising that a strict comparison of the Society's income and expenditure with that of the previous year is hardly possible. The income, although somewhat smaller than was anticipated a year ago, has not fallen off as much as might reasonably have been expected.

The income from all sources for the year is £8,122 4s. 5d., as against £9,235 14s. 1d. in 1913 and £8,120 12s. 3d. in 1912; the corresponding expenditures are £8,036 2s. 2d., £9,473 1s. 8d., and £7,944 10s. 8d. This leaves a small balance of £86 2s. 3d., being an excess of income over expenditure as the result of the year's working.

The chief falling-off in our ordinary sources of income is in the small amount received as life composition and in admission fees, of which the first is £140 and the second £76 less than last year. As was pointed out a year ago, both the income and the expenditure for 1913 were exceptionally large, owing to the sale and to the printing of Vol. V. of the Decennial Index. The further sales of this have now almost defrayed the cost of printing both parts.

It is amongst the various items in the expenditure of the Society that the effects of the war are most notable. The activity of the Society and of chemical science throughout the world is reflected in the pages of the Journal. For printing alone, the first six numbers of the Journal cost £1,729 6s. 2d., instead of £1,413 8s. 5d.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1914.

Liabilities.

	£ s. d.	£ s. d.
To Subscriptions received in advance		189 0 0
,, Sundry Creditors		1419 5 10
,, Research Fund :—		
As per last Balance Sheet	10531 13 2	
Add Excess of Income over Expenditure for the year	93 17 5	
		10625 10 7
,, Chemical Society : Excess of Assets over Liabilities :—		
As per last Balance Sheet...	20332 1 9	
Add Excess of Income over Expenditure for the year	86 2 3	
		20418 4 0
		£32652 0 5

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212 8 6	
£1050 London and North Western Railway 3 per cent. Debenture Stock	839 12 0	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent. Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£4341 Midland Railway 2½ per cent. Preference Stock	3572 2 5	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460 13 6	
£1200 North British Railway 3 per cent. Debenture Stock	1033 11 0	
£700 Canada 2½ per cent. Stock, 1930/50	704 8 6	
(Estimated present value of Investments, £17324 7*s.* 6*d.*)		21001 19 11
,, Sundry Debtors :—	£ s. d.	
Advertising Account	59 1 6	
Less Commission accrued	5 7 2	
	53 14 4	
Optical Society	9 9 0	
Messrs. Gurney & Jackson	557 12 2	
Telephone Deposit	1 0 0	
		621 15 6
,, Subscriptions in Arrear, £491 10*s.* Estimated to realise		320 0 0
,, Insurance paid in advance		25 14 1
,, Cash at Bank	35 4 8	
,, Cash in hand	21 15 8	
		57 0 4
,, Research Fund :—		
Investments (value when acquired):		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587 18 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049 15 11	
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£1365 Midland Railway 2½ per cent. Debenture Stock	1010 0 9	
£806 Victoria 3 per cent. Stock	706 6 2	
(Estimated present value of Research Fund Investments. £9114 11*s.* 9*d.*)	10366 17 7	
,, Cash at Bank...	258 13 0	
		10625 10 7
		£32652 0 5

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				157	0	0
,, Admission Fees				564	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1914	296	0	0			
,, during 1914 ,, ,,	4495	0	0			
,, ,, ,, ,, 1913	322	0	0			
,, ,, ,, ,, 1912 and previous	22	10	0			
	5135	10	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	360	0	0			
	4775	10	0			
Add Arrears at date: 1914, £474; 1913 and previous, £17 10s., estimated to realise as per Balance Sheet	320	0	0			
				5095	10	0
,, Lady Subscribers				7	10	0
,, Investments:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock	221	1	7			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	29	12	6			
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	42	15	6			
,, £1400 India 2½ per cent. Stock	32	17	1			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	56	7	6			
,, £4341 Midland Railway 2½ per cent. Preference Stock	102	1	7			
,, £1200 Leeds Corporation 3 per cent. Stock	33	15	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	42	3	9			
,, £1200 North British Railway 3 per cent. Debenture Stock	33	16	2			
,, £700 Canada 3½ per cent. Stock 1930/50	22	19	5			
,, Income Tax Recovered	35	13	10			
,, Interest on Deposit Account	11	11	9			
				664	15	8
,, Publication Sales:—						
Journals	1103	12	6			
Proceedings	36	16	6			
Collective Index	213	1	11			
Memorial Lectures	37	14	3			
Library Catalogue	1	6	9			
Atomic Weight Tables		1	9			
Jubilee Volumes	2	8	9			
Annual Reports on Progress of Chemistry	149	3	0			
List of Fellows	2	0	0			
	1546	5	5			
Less Publishers' Commission	145	5	4			
				1401	0	1
,, Proceeds of Advertisements in Journal	£213	9	0			
Less Commission	18	13	11			
				194	15	1
,, Miscellaneous Receipts					8	1
,, Subscriptions from other Societies				37	5	6
				£8122	4	5

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

23, Queen Victoria Street, E.C.
March 9th, 1915.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1914.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal and Proceedings :—		
Salary of Editor, including Indexing	595 0 0	
Salary of Sub-Editor and Assistance	212 10 0	
Editorial Postages	25 17 0	
Abstractors' Fees	490 0 5	
Printing of Journal	3230 6 6	
Banding	58 12 8	
Printing of Advertisements	63 7 7	
Wrappers and Addressing	56 7 4	
Distribution of Journal	602 0 8	
Authors' Copies	205 1 2	
Insurance of Stock	5 4 0	
Printing of Proceedings	224 10 8	
Banding ,,	11 8 8	
Distribution ,,	53 0 0	
		£833 6 8
,, Annual Reports on the Progress of Chemistry		401 10 7
,, Binding Memorial Lectures		12 10 0
,, Purchase of back numbers of Journal		24 3 8
,, List of Fellows		73 1 6
,, Addressograph Machine		44 5 0
,, Library Expenses :—		
Salary of Librarian and Assistant	213 12 0	
Books and Periodicals	187 13 3	
Binding	47 4 2	
		448 9 5
,, Indexing for International Catalogue		30 0 0
,, Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological		10 0 0
,, Faraday Medal and Lecture Expenses		34 5 8
,, Administrative Expenses :—		
Salary of Staff	364 18 0	
Wages (Commissionaire, Housekeeper, and Charwoman)	168 16 6	
Coal and Lighting	44 3 11	
House Expenses and Repairs	130 0 3	
Furniture	15 12 7	
Tea Expenses	38 14 10	
Insurances	26 8 9	
Accountants' Charges	21 0 0	
Commission on Recovery of Income Tax	1 15 9	
Printing	118 19 8	
Stationery	54 5 5	
Postages	107 13 5	
Miscellaneous Expenses	32 0 7	
		1124 9 8
,, Balance, being excess of Income over Expenditure carried to Balance Sheet		86 2 3
		£8122 4 5

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—JAMES J. DOBBIE.
ALEXANDER PEDLER.
A. LIVERSIDGE.

Research Fund Income and Expenditure Account for the Year ended 31st December, 1914.

Income.

	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	37 12 6	
£4400 Metropolitan Consolidated 3½ per cent. Stock	144 10 9	
£1034 Great Western Railway 2½ per cent. Debenture Stock	24 6 4	
£1142 16*s.* New South Wales 3 per cent. Stock	32 4 4	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	31 12 10	
£1365 Midland Railway 2½ per cent. Debenture Stock	32 1 3	
£806 Victoria 3 per cent. Stock	22 13 4	
		325 1 4
,, Repayments of Research Grants:—		
F. C. Garrett	10 0 0	
H. Stephen	5 0 0	
C. Smith	2 4	
R. Robinson	15 0 0	
W. J. Jarrard	1 7 4	
F. W. Caton	2 6 9	
V. Steele	10	
F. D. Chattaway	15 8	
N. P. McCleland	5 0 0	
		39 12 11
,, Income Tax Recovered		19 0 2
		£383 14 5

Expenditure.

By Grants to—	£ s. d.		£ s. d.	£ s. d.
M. P. Applebey	8 0 0	*Brought forward*—	167 0 0	
C. C. Bissett	30 0 0	J. N. Rakshit	5 0 0	
G. Blackstock	5 0 0	R. Robinson	15 0 0	
F. Challenger	16 0 0	C. Smith	5 0 0	
G. W. Clough	8 0 0	F. B. Thole	5 0 0	
G. Dean	5 0 0	E. R. Thomas	8 0 0	
F. P. Dunn	10 0 0	E. E. Turner	6 0 0	
A. C. Dunningham	10 0 0	E. Vanstone	10 0 0	
A. E. Dunstan	10 0 0	C. Weizmann	10 0 0	
A. Forster	5 0 0	R. R. Baxter	7 0 0	
W. H. Gibson	5 0 0	R. G. Fargher	7 0 0	
J. Heyrovsky	6 0 0	C. F. Hawkins	5 0 0	
W. J. Jones	5 0 0	B. Lambert	8 0 0	
F. E. E. Lamplough	20 0 0	M. S. Leslie	10 0 0	
G. Martin	5 0 0	R. W. Merriman	5 0 0	
F. M. G. Micklethwait	5 0 0	E. Robinson	7 0 0	
J. E. Myers	4 0 0	H. A. Scarborough	7 0 0	
J. E. Purvis	10 0 0			
				287 0 0
Carried forward—£167 0 0				
,, Commission on Recovery of Income Tax				19 0
,, Advertisements				1 18 0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				93 17 5
				£383 14 5

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant

23, Queen Victoria Street, E.C.
March 9th, 1915.

Approved—JAMES J. DOBBIE.
ALEXANDER PEDLER.
A. LIVERSIDGE.

for the same period in 1913, which corresponds to an increase of from £600 to £650 for the year. The Council in June, therefore, decided to raise the selling price of the Journal from £2 to £3 per annum from 1915 onwards. The diminution in the research work in this country, as well as on the Continent, combined with the difficulty in obtaining foreign periodicals for abstracting purposes, has led in the later months of the year to an unprecedented decrease in the size of the monthly parts of the Journal. How this has reacted in diminishing the cost will be easily understood when it is stated that the accounts for printing the November and December numbers, respectively, were £79 15s. 6d. and £148 4s. 7d. less than for the corresponding months of 1913, and that the abstractors' fees for the latter half of the year were also less by £131 11s. 4d. The total cost of the Journal and Proceedings for 1914 was £5,833 6s. 8d., as against £5,769 18s. 3d. in 1913, an increase of £63 8s. 5d., or only about one-tenth part of the increased cost which seemed to be inevitable before the outbreak of war. One item in which considerable saving has been effected is "wrappers and addressing," which for the Journal in 1913 amounted to £117 10s. 7d.; by means of an addressograph machine, which has been in use for only four months, this has been reduced to £56 7s. 4d., and it is expected that approximately £100 per annum may be saved in this way. The house expenses and repairs seem unduly large, but this is due to the account from H.M. Office of Works for structural alterations involved in fitting up a basement room for the extension of the Library having been rendered this year instead of in 1913.

Owing to the war, the grants from the Research Fund are abnormally low, amounting in all to £287, and of this already some has been returned, at least one recipient having gone to the Front. The income of the Fund from investments, as usual, amounts to about £343, and almost £40 has been returned, so that an unexpended excess of income over expenditure of £93 17s. 5d. has been added to the balance in hand.

Some idea as to the growth of the Society and its work during the tenure of office of the present Treasurer may be gathered from the following figures:

	1904.			1914.			Increase.		
	£	*s.*	*d.*	£	*s.*	*d.*	£	*s.*	*d.*
Income	6,700	5	8	8,122	4	5	1,421	18	9
Expenditure	5,982	14	6	8,036	2	2	2,053	7	8
Balance	717	11	2	86	2	3			
Cost of Journal	3,962	9	7	5,544	7	4	1,581	17	9
Cost of Proceedings...	215	14	2	288	19	4	73	5	2
	4,178	3	9	5,833	6	8	1,655	2	11

It ought to be pointed out that the expenditure in 1904 includes £371 1s. 8d. due to Vol. IV. of the Decennial Index; if this were not included, the excess of income over normal expenditure would be £1,088 12s. 10d.

One item which appeared for the first time in the accounts for 1905, and which has varied in each succeeding year from about £400 to £500, is that of "The Annual Reports on the Progress of Chemistry." Whilst their publication has added considerably to the difficulties in making both ends meet, it is universally acknowledged that the money laid out in this way is well spent, and that these annual volumes are much appreciated by the Fellows and other students of chemistry.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Professor W. PALMER WYNNE, seconded by Mr. A. CHASTON CHAPMAN, and acknowledged by Professor A. HARDEN.

In presenting the Longstaff Medal for 1915 to Dr. Forster, the PRESIDENT said:

"In the wide range of organic chemistry there is probably no substance which has excited more interest among chemists than camphor, and the investigation of the properties of this substance and of the remarkable relationships of its various derivatives has indeed been a brilliant achievement. Many years of difficult experimental work and the combined efforts of an army of investigators were necessary before the complex changes which camphor and its derivatives undergo could be thoroughly understood, and the fact that all these intricate changes may be explained with the aid of the ordinary formulæ of organic chemistry is, it seems to me, one of the most striking proofs of the soundness of the principles on which our present views of the structure of organic substances are based. It may be said that the chemistry of camphor has now reached a definite stage, and it is therefore fitting that we should confer the Longstaff Medal on one who has done so much to contribute to the solution of the nature of this extraordinary substance. I find that Dr. Forster commenced his studies on camphor in 1895, and from that date until the present time he has communicated to our Journal a long series of valuable papers on the subject, which are characterised by their careful conception, brilliant experimental accomplishment, and lucid exposition.

"In addition to these papers, Dr. Forster has, during the last few years, been actively engaged on a difficult and important series of investigations of the triazo-derivatives, and particularly of those

derivatives which are obtained by the action of sodium azide on the corresponding halogen derivatives, and the results he has obtained in this field also have been of unusual interest. Throughout the whole of this time he has associated himself with many of the advanced students who have come under his supervision, and has thus been able to train them in the accuracy of his methods and to impart to them some of his enthusiasm.

"Dr. Forster, it is a great pleasure to me to convey to you the congratulations of the Council, and, in handing you the Longstaff Medal, I should like to express the hope that you will still be able to continue your work, and that we may look forward to a further series of those accurate and important investigations with which your name is so closely associated."

Dr. Forster acknowledged the gift.

The PRESIDENT then delivered his address entitled, "The Position of the Organic Chemical Industry." Professor H. E. ARMSTRONG proposed a vote of thanks to the President for his services in the Chair during the past two years, coupled with the request that he would allow his address to be printed in the Transactions. The motion was seconded by Sir WILLIAM TILDEN, and carried with acclamation, acknowledgment being made by the President.

The report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the year 1915–1916:

President.—Alexander Scott, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., Pres.R.S.; Sir James Dewar, M.A., LL.D, F.R.S.; Harold Baily Dixon, M.A., Ph.D.. F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry Enfield Roscoe, D.C.L., LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

Vice-Presidents.—Herbert Brereton Baker, M.A., D.Sc., F.R.S.; Peter Phillips Bedson, M.A., D.Sc.; Horace Tabberer Brown, LL.D., F.R.S.; Charles Thomas Heycock, M.A., F.R.S.; Francis Robert Japp, M.A., LL.D., F.R.S.; Richard Threlfall, M.A., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, D.Sc., Ph.D., F.R.S.

Ordinary Members of Council.—George Barger, M.A., D.Sc.; the Rt. Hon. the Earl of Berkeley, F.R.S.; David Leonard Chapman, M.A., F.R.S.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Thomas Martin Lowry, D.Sc.; F.R.S.; William Macnab; Kennedy Joseph Previté Orton, M.A., Ph.D.; Robert Henry Aders Plimmer, D.Sc.; Edward John Russell, D.Sc.; George Senter, D.Sc., Ph.D.; John Millar Thomson, LL.D., F.R.S.; Jocelyn Field Thorpe, D.Sc., Ph.D., F.R.S.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 25th, 1915.

By WILLIAM HENRY PERKIN, Ph.D., Sc.D., LL.D., F.R.S.

The Position of the Organic Chemical Industry.

THE subject which I have chosen for my Address on this occasion must always be regarded as of the highest importance, not only to this Society, but also to the country at large, because of its intimate connexion with the prosperity of so many of our largest and most successful industries. It is a subject which has been discussed over and over again at scientific societies, in scientific journals, and particularly in the newspapers by chemists, manufacturers, politicians, and the general public. In his valuable presidential address to this Society in 1907, entitled "The Position and Prospects of Chemical Research in Great Britain," Professor Meldola had much to say about the bearing of research on the position of industry, and, in 1909, the same writer discussed very fully the question of the value of education and research in connexion with applied chemistry in his presidential address to the Society of Chemical Industry. It would therefore seem scarcely necessary that I should take up your time by bringing these matters to your notice again. I do not propose, however, to apologise, partly because I am of the opinion that a summary of the position of the organic chemical industry in as few words as possible will not be out of place and may be useful, but more particularly because, in spite of the large amount of literature bearing on the subject, I feel convinced that the causes of the decadence of this industry in this country are still imperfectly understood.

The seriousness of the position is readily grasped when it is borne in mind that the value of the colouring matters consumed in this country is at least £2,000,000 per annum, and that more than 90 per cent. of this quantity comes from Germany, and, when it is remembered that these dyes are essential to textile industries representing at least £200,000,000 per annum, and employing more than 1,500,000 workers, it is easy to see to what an alarming extent these great industries are in the grip and power of the Germans. There are, of course, many other industries which depend on colouring matters for their existence, such as, for

example, the wallpaper, the printing, and paint industries, to all of which lakes and pigments are absolutely essential, and of late years almost the whole of these have been imported from Germany. Again, the enormous quantities of organic chemicals required for photographic purposes, such as, for example, pyrogallic acid, hydroquinone, metol, and many other similar developers, the natural and artificial products employed in such huge quantities in the manufacture of scents and perfumes, the synthetical and other drugs which have in some ways revolutionised medical science, and also many of the more important disinfectants have been almost exclusively made in Germany. We may add to this list the vast trade in fine chemicals, for here we are again completely outclassed, since there are no firms in this country which can compete with Kahlbaum, Merck, Schering, de Haen, and a host of others either in the range or the purity of their products, and it has long been our habit to import almost all our organic fine chemicals from Germany. It may indeed be said that Germany has no competitor worth considering in the whole domain of organic chemical industry. That we should have allowed trades of such magnitude to pass almost completely into the hands of a foreign nation seems incredible, and, as the inevitable result, we are face to face with the serious position that, the foreign supply having stopped, stocks are rapidly vanishing and prices are rising to such an impossible level that the progress of several of our industries is greatly hampered. Indigo, perhaps the most essential of all dyes, is manufactured entirely by the great German colour works, and the stock in this country a few weeks ago was so low that the price rose to at least ten times what it was before the war; the same thing is happening in other cases, and many dyes cannot be obtained at any price. Obviously we must take warning, and not allow, in the future, our textile and so many other similar industries to be controlled in this way by the foreigner, and to be in danger of being brought to a standstill.

How are we to explain the fact that we have allowed some of our most important industries to get into this critical condition, and what do we propose to do to remedy this state of things and prevent any recurrence in the future? No one doubts for a moment that the wonderful opportunity of establishing a great national industry, due to the discovery of the aniline dyes in this country, has been allowed to escape us, and various reasons have been put forward to explain the loss of the colour industry. There can be no doubt that a good many different causes have been at work. One of the main reasons for our position is that we as a nation, and our manufac-

turers in particular, have failed to understand the extreme complexity of the scientific basis of organic chemical industry, and have concluded that this industry could be carried on much in the same way as the manufacture of sulphuric acid, caustic soda, and other heavy chemicals. The manufacturer has always been unwilling to acknowledge that neglect of science in his works is the real cause of his failure to retain the colour industry in this country, and has therefore put forward all sorts of other reasons to explain his want of success.

Thus it has been urged repeatedly that our patent laws were greatly to blame, and that these laws were such that an English patent was no protection, and that so soon as anything new had been discovered in this country the Germans at once set to work to manufacture it.

Even if this were true, and there may be some truth in it, it does not explain why the Germans were able to obtain their raw material as they did in this country, to transport it to Germany, and then to send the dye over here, and at the same time to make a handsome profit out of the transaction. Again, it has been urged that the obstacles to the use of pure alcohol which existed at the end of the last century played a great part in bringing about the decadence of the coal-tar colour industry in this country. Possibly there has been some hardship in special cases, but a Departmental Committee of the Board of Trade took evidence from a large number of experts in this country and in Germany, and issued a report on "Industrial Alcohol" in 1905, and the Committee arrived at the conclusion that, as a statement of historical fact, the assertion that the coal-tar industry has been lost to this country on account of obstacles to the use of pure alcohol is devoid of substantial foundation. Of late years the restrictions on the use of duty-free alcohol have been so relaxed and the denaturants which may be employed are of such a wide range, including as they do the actual articles to be manufactured,* that there is probably at the present time less difficulty put in the way of the manufacturer here than is the case in Germany.

It is quite obvious that other reasons than those I have just mentioned must be found to account for the gradual transference of the coal-tar industry to Germany. The decadence of this industry and its gradual transference to Germany may be said to have begun during the period 1870–75. It was in 1874 that the works of Perkin and Sons at Greenford Green was sold to the firm of

* For example, the manufacturer of pure ether may denature the alcohol he uses by the addition of a little sulphuric acid, and, in the case of diethylaniline, this substance or aniline may be used as the denaturant, and so on.

Brooke, Simpson, and Spiller, and these works were then in the most prosperous condition, and much in advance of anything that existed in Germany.

One reason for the sale was my father's natural dislike to an industrial career, and his desire to devote himself entirely to pure chemistry. There was, however, a much more weighty consideration which played the really important part in his decision to dispose of the works.

It was recognised—and as the subsequent history of the coal-tar industry has shown, correctly recognised—that the works could not be carried on successfully in competition with the rising industry in Germany unless a number of first-rate chemists could be obtained and employed in developing the existing processes, and more particularly in the all-important work of making new discoveries. I remember quite well that inquiries were made at many of the British universities in the hope of discovering young men trained in the methods of organic chemistry, but in vain. There cannot be any doubt that the manufacturer of organic colouring matters during the critical years 1870–80 was, owing to the neglect of organic chemistry by our universities, placed in a very difficult and practically impossible position. At that time organic chemistry was not recognised by the older universities, and the newer universities, which have since done so much for the progress of science, had not come into existence. It is surely remarkable that the study of so important a subject as organic chemistry should not only have been practically ignored by our universities in the past, but that even at the present day it does not flourish in the way it does in almost every university and technical school in Germany.

This seems to me the more remarkable when it is borne in mind that all problems connected with life, either in the animal or vegetable kingdom, are essentially problems which depend on, and are largely controlled by, organic chemistry, and it is therefore clear that little progress can be made towards the solution of such problems until the processes of organic chemistry are clearly understood. Quite apart, therefore, from its industrial aspect, organic chemistry must, from the purely scientific point of view, always be regarded as a branch of science of the very highest interest and importance.

If the record of our universities is examined, it is at once obvious that many of these famous places, and more particularly the Universities of Oxford and Cambridge and the Scottish Universities, contributed practically nothing to the advancement of organic chemistry during the latter part of the last century, and their

output of research in this subject is still far less than it ought to be. It is difficult to understand why our universities should so persistently hold aloof from progress, and should so often entirely fail to gauge the importance of leading the way in new developments, on which, after all, in many cases the welfare of the country depends. How very different is the picture exhibited by the attitude of the German universities towards organic chemistry during the critical period I have mentioned.

So soon as the importance of organic chemistry became apparent, great teachers, such as Liebig and Wöhler, Kekulé and Baeyer, founded schools specially devoted to the subject, and they and their pupils then began to publish that wonderful series of classical investigations which laid the foundations on which the superstructure has since been raised.

The value of the example of these great teachers and of the system of research which they had initiated soon became generally appreciated by the universities in Germany, and every effort was made, by the establishment of laboratories supported by adequate grants from the various States, to help forward the new movement. The step which, in my opinion, did more than anything else to bring about the wonderful development of organic chemistry in Germany was the provision that research must be an essential part in the training of every German student of chemistry. It is well known that the student who studies in a German university with the view to obtaining the Ph.D. degree must, after completing three years of systematic study, spend at least one year, and usually two years, in carrying out a research on some subject suggested to him by the professor or one of the Privatdozenten attached to the laboratory, and must then write up the results and present them in the form of a dissertation. In other words, every student is brought into contact with research as a matter of course, and it is made quite clear to him directly and indirectly that his future career as a teacher or as a works chemist depends mainly on his ability as an investigator. It is no uncommon thing, in large laboratories such as those of the Universities of Berlin, Munich, and Leipzig, to find fifty students engaged in original work, and these are the men who, after taking their degree, are directly available for the research laboratories of the manufacturer. In this country the student obtains his B.Sc. degree with Honours, merely as the result of a three years' course of systematic study of the stereotyped kind, and although a certain number remain for a further year, the majority are under no obligation to do anything in the nature of an original investigation during their career at their university.

Since then the necessity for research as an essential part of the training of the science student is not insisted on, it is not surprising that the output of original work in this country has in the past been small compared with that of Germany, and that the supply of able research chemists is so limited. I am sure there are many who will agree with me when I suggest that the German system is, in this respect, worth copying, and that the B.Sc. degree of our universities, and certainly the B.Sc. with Honours, should not be conferred except on those who have gone through a course of research as an essential part of their training.

A change in this direction* would not only mean that our graduates were better trained; it would also ensure that a supply of first-rate chemical ability was always available to assist in the development of the industries of the country. If the universities of our country had, at the time the Greenford Green works changed hands and for some years afterwards, trained able research chemists and placed them at the disposal of the manufacturer, there can be no doubt that these works as well as others would still be in existence and flourishing, and that we should have kept the coal-tar colour industry here, and it is precisely for this reason that I express the opinion that the universities, more perhaps than the manufacturers, were to blame for the loss of the industry.

In almost every direction and to a far greater extent than has been the case in any other country, Germany has recognised the value of the closest possible contact between the industries and the universities. In Germany the majority of the professors and Privatdocenten are in close touch with the large factories, and spend part of their time in solving technical problems which they either devise themselves or which may be submitted to them by the manufacturer.

I have it on the authority of several of the best-known directors of German works that the atmosphere of the university laboratory is much more suitable for discovery than that of the works, and that, as a fact, many of the most valuable discoveries which subsequently proved to be of the highest technical importance have been made in university laboratories and transferred to the works as the result of the intimate connexion I have just described. Moreover, when it is remembered that the important dyes, mala-

* The necessity for some such change is being gradually recognised. In our modern Universities, the M.Sc. degree can now only be obtained on the presentation of a thesis involving original work, and the institution of research degrees in Oxford and many other of our Universities is also a step in the right direction, but the proportion of our graduates who engage in research in these circumstances is still very small, and not comparable with the number of German chemists who qualify for the Ph.D. degree.

chite green, the phthaleins, artificial alizarin, and indigo, and the pharmaceutical products antifebrin and antipyrine, to mention only a very few cases, were discovered in university chemical laboratories, it is quite clear that there is much truth in the statement of the works directors. Close association of the universities with the industries does not exist to any extent in this country, and is one of the things we have to aim at in the future, however distasteful this may appear to some of our academic circles. Systems of training and methods of teaching which may have been useful centuries ago, but have become antiquated, must, in these days of acute competition, give place to methods that are more in accordance with existing requirements and the practice of other nations; otherwise we are bound to fall behind in the race.

It must, I take it, be assumed that the aim of the university is to acquire the best scientific ability for its professoriate and teaching staff, and therefore the home of the best scientific research talent must always be the university laboratory; it is therefore quite clear that close association between these laboratories and the works must be of great advantage to industry. Such a connexion cannot fail to be of great value also to the university, for it must result in the manufacturer taking a keen interest in the welfare of the department with which he is associated; he will willingly provide material from his works for teaching and research, and subscribe liberally to the resources of the department, and no scientific laboratory—chemical, physical, or engineering—can do good work unless it is liberally supplied with material and funds.

It has often been suggested to me that a professor who is engaged in solving problems of a technical nature will have no time for other scientific research work, and that, since results of technical value must often be kept secret and may never be published, the reputation of his department will suffer. Experience shows, however, that such is not the case, for there is little, if any, diminution in the output of research work in pure science from the German laboratories as the result of this system.

We must, I think, agree that one of the main reasons for the rise and development of the German chemical works is the appreciation on the part of the manufacturer of the value of science in connexion with industry, and the recognition of the great importance of a close alliance between the works and the research laboratories of the universities and leading technical institutions of the country.

My view is that contact with the research department of a large

works must always be stimulating; problems are encountered, many of them of great scientific interest, which would never suggest themselves in strictly academic circumstances, and as one of the results, the tendency, which is always present under existing university conditions, for the professor to become an academic fossil and unproductive, is postponed. Again, we are all aware how difficult it often is to find suitable research subjects for the budding chemists under our charge, and contact with the research departments of a flourishing works cannot fail to suggest subjects for investigation which are eminently suitable to occupy the attention of young men, many of whom will ultimately take up technical work. I look forward to the time when the scientific staffs of our universities and technical schools will not only be available for industrial research, but will be encouraged by those in authority to undertake such work, for I am quite certain, and indeed it is very generally admitted, that the association of the best academical talent in the country with the technical laboratories of the works can only be of the highest mutual benefit.

After all, this kind of thing is quite common in the case of the engineering departments of our universities and technical schools, and, if the system works well in the case of engineering, there is surely no reason why it should not be equally successful in the case of chemistry.

It should not be a difficult matter to arrange the conditions under which such work may be undertaken, but it ought to be made quite clear to all concerned that the only work which the universities will entertain is research, and that nothing of the nature of analysis or ordinary routine commercial work, or work in connexion with patent or other litigation, will be considered. I am convinced that, when the new development has been given a fair trial, the difficulties which some are inclined to urge against it will be found to be more apparent than real. While, then, I have been pleading for closer contact between the universities and the industries, and have suggested that the existence of such an alliance has been an important factor in the development of the vast organic chemical industry in Germany, it must be remembered that many other influences have been at work to bring about this result.

Our competitors have, from time to time, given their opinion as to the reasons for the transference of the organic chemical industry from this country to Germany, and, as such views cannot fail to be instructive, it will not be out of place if I quote one such utterance. On the occasion of the jubilee of the discovery of mauve, in 1905, Dr. Duisberg, one of the best known directors of the

colour works of Bayer & Co., in Elberfeld, went fully into this question, and I propose to read a few extracts from his remarks which have a special bearing on this matter. Dr. Duisberg said: "You inquire further, and wish to know how it is that the German soil, in which the coal-tar colour industry has grown so powerful, varies from English soil; what particular conditions were there which had been so advantageous for its fructification; whether it was not eventually possible to produce artificially the same conditions also in England, and that here also in the land of its birth those rich and golden fruits could not be gathered, the harvest of which is reaped by Germany year by year. I do not believe in such acclimatisation in England, at least for the present. No other industry requires so much uniformity of thought and action, science and practice, as organic chemistry and the organic chemical industry."

"In Germany, not only has chemical science developed to a considerable extent, but at the same time the technique of organic chemistry has flourished. Both have stimulated and vitalised each other, and both have supported each other. Such was not the case in England. Although the Englishman is in general practical, he is wanting in that peculiar quality which we Germans are remarkable for, that is, not perseverance, but patience and the power of waiting for success. For all the Englishman does he expects soon to be compensated in hard cash."

Continuing, Dr. Duisberg used the following words, which are particularly interesting in view of the present crisis. "But you will say, when the problems have been solved, and when the patents have run out and the manufacture is free to everyone, 'Why should not the English and foreign works decide to cope with the German firms and compete against them?"

"In my opinion this would be futile, and would be of no avail. Even in Germany, where, as we have seen, the conditions are the most favourable, it would now be scarcely possible, or at least be a singular coincidence if a manufacturer, although possessed of energy and capital, should succeed in building up a new firm in the colour line so as successfully to compete against the existing powerful works. Whereas, therefore, the conditions in England for many industries, such as for the mining industry, for spinning and weaving, not forgetting inorganic chemistry, are far more advantageous than in Germany, the latter country has the natural privilege in the organic chemical industry, and other nations should not envy her in this, but leave it to her."

It is because we have acted in the manner recommended by Dr. Duisberg, and have left the coal-tar colour industry to

Germany, that we find ourselves in the present grave and serious position.

Views similar to those of Dr. Duisberg have been expressed in many quarters, and Lord Moulton, in an address to the Royal Society of Arts on December 3rd of last year, gives an example which is also very much to the point. "I read," he said, "the other day with bitter feelings the address of one of the ablest industrial chemists in the world—the head of one of the German chemical industries—who, talking about this very subject said: 'England talks not only of holding her own in the war, but of beating us in the chemical industry. She cannot do it, because the nation is incapable of the moral effort of taking up such an industry which implies study, concentration, patience, and fixing the eye on distant consequences, and not merely on the monetary result.'" Lord Moulton himself puts the matter in this way: "Some fifty years ago organic chemistry opened up a domain of industrial wealth that he could only compare to that opened up by the discovery of steam power. He had been able to come to but one conclusion—that, either from being too well off or from sluggishness of intellect, or from the fact that the capital of the country had passed into the hands of people who were unwilling either to learn or to think, England had abstained almost entirely from an attempt to reap the rich harvest open to the industrial world by the advance of organic chemistry." In his address delivered in the Town Hall, Manchester, on December 8th, 1914, Lord Moulton said: "Gentlemen, we have to look the truth in the face. It (the loss of the coal-tar colour industry) was for no other reason than that the English dislike study. The Englishman is excellent in making the best of the means at his disposal, but he is almost hopeless in one thing. He will not prepare himself by intellectual work for the task that he has to do. Now there is the cause, and, so far as is material, the sole cause of the German supremacy. Is that a cause which must permanently operate? The answer is, of course, 'No.' But it is for us to reform ourselves; otherwise no relief can come."

I have ventured to read these short extracts because they contain the gist of the matter, and because I cannot think of any words which might describe the position better.

If, then, we accept the enormous technical importance of organic chemistry, and recognise, as Lord Moulton puts it, that the industry is so vast that it can only be compared with that opened up by the discovery of steam power, and if we decide that we are not going to allow—as Dr. Duisberg suggests that we should—all this wealth and prosperity to pass entirely into the hands of

a foreign country, what course must our manufacturers adopt in order to get a share of this? I have already said, and everyone will agree, that they must, in the first place, make up their minds so to conduct their works that research is going on unceasingly; no works can possibly flourish which is content to manufacture only well known colours, and it is only by the discovery of new colours and other products that manufacturers can hope to get a satisfactory return on their capital. The manufacturer must therefore see that his laboratories are properly equipped, and well supplied with research chemists of ability who have had a sound scientific training, and also some experience in the methods of research. All this, however, will avail little unless he has a scientific leader in his works who is able to direct the investigations of his young staff in the right channels.

Students of mine who have entered chemical works have frequently complained to me that there is no one over them qualified to direct their investigations, and that original work seems to be considered of secondary importance, and only to be indulged in when there is nothing else in the works to occupy the attention of the chemist.

So far as I am aware, there is not a single colour works in this country which has a really brilliant scientific head; by which I mean a chemist of wide scientific experience, and with the knowledge and ability to direct research, and this is a very serious state of things, and quite incompatible with chemical efficiency.

I have long thought that the want of an able scientific head is one of the most obvious reasons why our colour works are in such an unsatisfactory condition. The success of a business based on science must often be essentially the work of a single, brilliant, scientific man, just as the success of a great school rests with the headmaster, and the reputation of a university laboratory depends on the ability of the professor.

If a works is fortunate enough to have the services of a distinguished scientific man, capable of initiating and carrying out original investigations, and who will not only be constantly making discoveries himself, but be able at the same time so to influence his young staff that they will follow in his footsteps, the success of such a works can never be in doubt. I am afraid, however, that it will be a long time before we can hope that our manufacturers will give up their old-fashioned rule of thumb methods and fully grasp the truth of this vital matter.

My experience of the manufacturer in this country is that he is usually merely a commercial person who does not like the expert, and especially the idea of giving the expert a prominent position

in the control of his works. Possibly the reason in many cases is ignorance of the value of science, but more probably it is due to the fact that being ignorant of science himself, he feels that if the expert is given too much prominence he must either study himself in order to understand the expert or leave the essential control of the business in his hands. Both these courses are distasteful to the ordinary commercial member of a board of directors; the expert is therefore relegated to the background, and the business comes to grief.

It would seem to be scarcely necessary to point out that, if a chemical works is to be successful, the first essential is that it must be under chemical control, and that every department must be in the hands of an expert; the board of directors may then be a mixed board, provided that steps are taken to ensure that chemical opinion is largely represented on it. The recognition of the soundness of this principle is one of the main reasons for the success of the German works.

Anyone who has had the opportunity of visiting the principal German dye works, as I have, cannot fail to have noticed that chemical control is everywhere; the heads of departments are always chemists, and the board of management invariably includes a large proportion of the abler chemical experts employed in the works. Not only do German business men understand that the control of a chemical works must be in the hands of the chemist, but they are also careful to remunerate their chemists liberally, and to give them a share in any new development they may initiate, with the result that many of their leading chemists are in receipt of salaries quite unheard of in this country.

When we ask the question whether we can adopt methods of a similar kind in this country we find ourselves at once face to face with very grave difficulties. Let us assume that the necessity for the chemical control of a chemical works is conceded, as conceded it must be, and that it is clearly understood that the next step is the discovery of improvements in every direction, such as the invention of dyes better than those already known, and the economical development of essential existing processes, then the first thing to be done will be for our universities to set to work to educate a supply of organic research chemists who will be able to undertake this work. This will mean that organic chemistry will have to flourish to a much greater extent than it does now, because the supply of organic research chemists available under ordinary conditions is a very small one, and scarcely sufficient to meet even the moderate demand which exists at the present time.

The extraordinary complexity of the theoretical side of organic

chemistry and the multitude of practical methods which have been developed by a host of able workers, mainly during the last fifty years, make such extraordinary demands on the memory, manipulative skill, and perseverance of the student that success can only be achieved by constant study and great determination to succeed. It is quite clear to me that those of our students who wish to become successful organic chemists must radically alter their methods, and devote more energy and concentration to the mastery of the literature of the subject, and particularly must spend much more time than they do now in the laboratory in order that they may acquire real skill, and get a thorough working knowledge of the essential processes connected with the complex and difficult technique of organic chemistry. During the years I was in Germany, work used to begin in the chemical laboratory at 8 o'clock and continue, with a brief interval for mid-day dinner, until six. In our modern universities many students also work long hours, and get through a large amount of valuable practical work, but in some of the older universities the custom is to do a short morning's work, to devote the larger portion of each afternoon to recreation, and then possibly to work in the laboratory for an hour or two in the late afternoon. It is obviously impossible that efficient work can be done under these conditions, for not only are the hours far too short, but the break in the afternoon spoils the continuity, and therefore the efficiency of the work.

Clearly this state of things must be altered because it is, I think, generally admitted that the best ability in the country is concentrated in the older universities, and it is precisely from this class of student that brilliant research work and the most marked originality ought to be expected.

Probably, if there were a closer connexion between the industries and the universities, students would more quickly appreciate the great amount of theoretical study, practical ability, and originality which is indispensable to the making of a successful research chemist for an organic chemical works, and recognise that the requisite technique can only be acquired as the result of long hours in the laboratory.

If the effort gradually to develop—it is not a question of immediately establishing—a thriving organic chemical industry in this country is to be seriously taken in hand, and not to be merely talked about, and if the requisite capital is forthcoming, it is obvious that what will be required before everything else will be a really able chemical staff, and there should, therefore, be a great opening in the near future for young organic chemists of ability.

It is unfortunate from this point of view that many, probably the large majority, of our young chemists are not immediately available, since most of them are at present engaged in military service, and therefore the evolution of an efficient chemical staff will be no easy matter. A small beginning may have to be made, but, if the manufacturer will continually bear in mind that chemical efficiency must always be the basis of all his calculations, there is no reason to doubt that success will come in the end, even though it may, and probably will, be very slow at first.

Soon after the outbreak of the war, the critical position brought about by the shortage of the dyes which are vital to both the cotton and wool trades, and the impossibility of importing further supplies from abroad, called for immediate attention. Urgent representations from dyers and calico printers and others engaged in trades which require large supplies of dyes, forced the Government to see that something must be done, and done as quickly as possible, to find a solution for the extraordinary situation that had arisen. A Board of Trade Committee was therefore appointed on August 25th with the Lord High Chancellor (Viscount Haldane) as chairman,* with instructions to consider the best means of obtaining for the use of British industry sufficient supplies of chemical products, and, after hearing the evidence of many of the more important producers and consumers, a small Committee, of which Professors Meldola and Green and I were members, was charged with the task of sifting the mass of evidence which had come forward from all quarters.

The chairman of this Sub-Committee—Lord Moulton—devoted a great amount of his time and energy and experience of German industrial conditions to the task of interviewing representatives of the industries which were affected by the stoppage of supplies from Germany, and, as the result of the report of the Sub-Committee to the larger body, a meeting of representatives of industrial firms and associations was held on December 10th at the Board of Trade, when the following resolution was passed unanimously: "That this meeting approves in principle of a national effort being made by the trade to increase the British supply of synthetic colours, and welcomes the assistance of His

* The other members of the Committee were Mr. John Anderson, Dr. George Thomas Beilby, F.R.S., Prof. James Johnston Dobbie, F.R.S., Mr. David Howard, Mr. Ivan Levinstein, Prof. Raphael Meldola, F.R.S., Mr. Max Muspratt, Prof. William Henry Perkin, F.R.S., Mr. Milton S. Sharp, Sir Arthur J. Tedder, Mr. Joseph Turner, and Mr. Thomas Tyrer, with Mr. Frank Gossling, B.Sc., as Secretary. Prof. Arthur George Green, M.Sc., was subsequently added to the Committee. I am indebted to Mr. Gossling for valuable suggestions in connexion with this address.

Majesty's Government for that purpose." A committee* was appointed, and shortly afterwards recommended a scheme which involved the formation of a joint stock company, having for its object the manufacture and supply of synthetic colours. Subsequently, the Government announced that they were prepared to assist such an effort in the following way: "If a limited company were formed on co-operative lines with a share capital of £3,000,000, the Government agree to advance to such Company £1,500,000, bearing interest at the rate of 4 per cent. per annum, and secured as a first charge on the assets and undertaking of the Company, and to be repayable in twenty-five years." The important proviso was, however, made that "the interest on the advance and a sinking fund for the repayment are to be payable only out of the net profits of the Company, but are to be cumulative." When this scheme was made public its reception was not cordial, and the application for shares fell far short of what had evidently been expected by its promoters. In explanation of this it should, in the first place, be quite clearly pointed out that neither the Board of Trade Committee nor the Sub-Committee had anything whatever to do with the preparation of the scheme, and it is certainly extraordinary that a Committee consisting entirely of business men, and which did not include a single chemical expert, should have been entrusted with the formulation of a scheme for the founding and developing of a chemical industry.†

Had a chemical expert been present I venture to think that such a scheme would never have been placed before the public. It is stated in the Memorandum of Agreement attached to the scheme that the Company has been incorporated for the purpose, among other things, of manufacturing and selling dyes, colours, and other chemical substances, which, previously to the war, were exclusively or principally manufactured in Germany, and no mention is made of what ought to be the main object of such a company, namely, the employment of a large staff of research chemists under leaders of ability for the purpose of making new discoveries in every possible direction.

It cannot be too strongly emphasised that it is not merely a question of producing the dyes which are required during the war; any company which is formed must be established in so

* The Committee appointed was Messrs. Lennox Lee (Calico Printers' Association), Milton S. Sharp (Bradford Dyers' Association), H. W. Christie (United Turkey Red Company), Chas. Diamond (English Sewing Cotton Company), G. Marchetti (John Crossley and Sons), and R. D. Pullar (J. Pullar and Sons).

† Compare Prof. Meldola's admirable letter in the *Times* of January 20th.

strong a position that it can expect to deal successfully with the keen competition which will be waged with the greatest severity by the Germans after the war.

The promoters of the scheme do not appear to have appreciated the difficulties of the situation, and obviously think that the manufacture of dyes in this country which previous to the war had been invented and produced in Germany is a matter which can quite easily be managed.

It seems to be imagined in many quarters that, in order to manufacture a dye which had previously been made in Germany all that is necessary is to follow the directions given in the patent dealing with that particular dye. No greater mistake could possibly be made. It is common knowledge that German manufacturers have for many years devoted large sums to the establishment of an efficient staff of patent experts, whose business it is so to word a patent that, whilst it satisfies the requirements of the patent laws of the various countries in which it is taken out, it only gives such information as is absolutely necessary, and contains no indication of the process which is used in the actual manufacture. In many cases patents are devised which are of no practical value, and are merely intended to mislead and throw competitors on the wrong scent.* The discovery of the most efficient method of working patented processes is therefore often a matter of great experimental difficulty, and may require many months of research. Any new company started with the object of manufacturing dyes which previously to the war had been made exclusively in Germany must therefore be prepared to employ a large staff of research chemists for a long period without any prospect of return in the way of dividends.

Further, it must always be remembered that the Germans have many years' start of the new Company, and have accumulated such vast experience of methods of manufacture, and more particularly of the recovery and economical use of by-products, that they are able to sell at a profit at very low prices. What the new Company has to face is, therefore, in the first place, the problem of working out methods of manufacture and the utilisation of by-products until they have arrived at the same state of efficiency as the Germans, and that, it seems to me, may be a matter of years. While this is being done, the new Company must also be busily engaged in training a large body of research chemists under the supervision of capable scientific leaders, so that the works may develop in as many new directions as possible, because the Com-

* This point is well dealt with by Prof. Jocelyn Thorpe, F.R.S., in a letter to the *Times* of February 2nd.

pany can only hope for permanent success if it pursues a policy of discovery and invention. Another point has also to be borne in mind, and that is that the Germans supply dyes and other products, not only to this country, but to practically all the other nations, and, in the event of a new company being formed on such large lines that it might prove to be a serious competitor, a German works could well afford to sell at cost price or at a loss in this country and make its profits in other lands until the new Company had been ruined. Lastly, if we are to be allowed to make dyes, etc., during the war according to patents belonging to the Germans, what is to happen after the war? Will the Company be still allowed to use these patented processes, or will the patents again become the sole property of the Germans, and be workable in this country only on the payment of royalties or licences? This matter has, no doubt, been carefully considered by the law advisers of the Government, but, so far as I know, no authoritative statement has been issued which makes this situation clear.*

Although it is a matter of so much congratulation that the Government, which in past years has paid practically no attention to science and the application of science to industry, should, at last, have recognised the necessity for intervening and in no uncertain fashion, I have been forced to the conclusion, largely for the reasons which I have just stated, that the Company founded on the lines of this first Government scheme could not be expected to be successful in achieving the object which we all have so much at heart, namely, the recovery and development of the organic chemical industry in this country. Since the application for shares

* Mr. Runciman made the following reference to this important point in Parliament on February 23rd last :—

"The success of the concern would depend largely on the way in which the German patents were administered. The Act passed last autumn as an emergency measure provided that the operators of German patents in this country should have a full chance of conducting them under licence, and it was the intention of the Government not to cripple this company when the war was over, but to give them every opportunity of making the most of German patents. They would leave over for discussion as between Germany and this country the payment of royalty in respect of these patents. There were English patents in Germany on which he hoped a royalty was being paid there. We should hand over these royalties if Germany would bargain fairly with us. But the operating of these patents which would be undertaken by the new company would proceed after the war was over without interruption and without hindrance."

If this statement means that, besides the arduous task of competing with the well-established German works. the new company may also have to pay royalties or licences to those works, then it is obvious that the difficulties of the situation will be greatly accentuated.

in the proposed Company was quite insufficient, the Government withdrew the scheme, and substituted for it an amended proposal, which is certainly in some respects an improvement.* The new proposal is to form a Company with a share capital of only £2,000,000, towards which the Government will make a loan for twenty-five years corresponding with the amount of the share capital raised, and up to a total of £1,000,000.

In addition, and with the desire to promote research, the Government have undertaken for a period of ten years to make a grant to the Company, for the purposes of experimental and laboratory work up to an amount not exceeding in the aggregate £100,000.

This amended proposal is another proof of the determination of the Government to meet the criticisms which were raised against the first scheme in a generous spirit, and to do all it possibly can to assist the efforts of the manufacturers in this country to place the organic chemical industry on a firm basis. If, then, I make certain criticisms of the new proposal, it must be clearly understood that I do not do so in any spirit of hostility to the scheme, but rather in the hope that the adoption of some modifications in the proposals may make the scheme workable and more likely of success. In the first place I hold that the scheme must be considered in the light of the criticisms which I have just advanced in connexion with the first Government plan, and I hope that these points will be clearly handled in any detailed statement of this or any subsequent scheme.

There are, however, other matters which call for comment. The grant for scientific research may be welcomed as a satisfactory addition to the old proposal, mainly because it shows that the Committee of users of dyes have at last found out that research is necessary if the new Company is to be a success. My own feeling, however, is that the Company ought to provide for research out of its ordinary capital as a matter of course, and should not require a special subsidy for this purpose.

A much better plan, I venture to think, would be to employ this grant to subsidise the research laboratories of those universities and technical schools which are willing to specialise in organic chemistry, and are prepared to train a certain number of research

* The members of the enlarged Committee which is responsible for the second scheme are Sir A. F. Firth, Bart., Sir Frank Hollins, Bart., Sir Mark Oldroyd, Mr. H. W. Christie, Mr. J. Clarkson, Mr. Charles Diamond, Mr. Kenneth Lee, Mr. G. Marchetti, and Mr. R. D. Pullar, and, in spite of Prof. Meldola's letter and other letters to the Press again did not include expert chemical opinion.

students with the definite view of their subsequently entering the service of the new Company. Supposing the new Company were to adopt the view which I have urged in this address, that closer connexion between the universities and the industries is most desirable, and were to work in conjunction with the staffs of some of the leading organic schools, it is quite obvious that the knowledge of the needs of the works which would result from this connexion would enable the staff to supply research students of exactly the type required by the works. Such research students would have been trained under the best scientific supervision which the country can provide, and at the same time they would enter the works with a considerable knowledge of the application of organic chemistry to technical operations, and be in a position to tackle with success research problems connected with new discoveries and new developments in the works. The plan of training research students under these conditions is, as I have already pointed out, the one which has long been adopted with such extraordinary success in Germany, and the large subsidies which the various States place at the disposal of their universities allow of the purchase of expensive apparatus and appliances which are outside the inadequate resources of most of the university laboratories of this country.

With regard to the kind of works it is proposed to organise for the manufacture of dyestuffs, etc., which previous to the war had been made in Germany, the following suggestions are contained in the explanatory statement attached to the first Government proposal, and which are, no doubt, also applicable to the newer scheme.

"To meet the difficulties of the present situation it is proposed to take over certain existing colour works, and use the plants to their full capacity for the manufacture of such dyes as are essential."

"Negotiations with Read Holliday and Sons, Ltd., have resulted in arrangements being made for the extension of their plant so as to secure a material increase in their output, and it is proposed that the new Company shall take over the business and undertaking of Read Holliday and Sons, Ltd., under an option which has been obtained. It is intended to negotiate for the acquisition of other businesses which it may be desirable to take over and extend, in the same way as that of Read Holliday and Sons, Ltd., and also to take steps to acquire a suitable site and erect and equip works thereon."

In dealing with this important matter it would be well carefully to consider the policy which the Germans have adopted with so

much success in the matter of the construction and arrangement of their works. I think that one of the things which must strike a visitor to a great German works more perhaps than any other is the order and cleanliness which reigns everywhere, and the obvious care which is taken that every manufacturing operation shall be efficient in every detail. This order and cleanliness is not confined to the section of the works which deals with organic products; the same state of things is to be observed in every part, as, for example, in the case of the large plants which deal with the manufacture of sulphuric acid, nitric acid, and other inorganic products. Perhaps the idea which is conveyed most vividly by works such as these, all of which are concerned with the manufacture of a very large number of products of widely different character, is that they are, after all, merely laboratories on a larger scale. A very different impression is got by an inspection of many of the colour works in this country, and it seems to me very doubtful policy to suggest the possibility of the acquisition of works of this kind, which are obviously not efficient, and could only be made so by pulling down and re-building. It may be said that the most efficient only will be taken over, but selection will be found most difficult, because, if the new Company proves a success, great pressure will be exerted by existing works in order to enter the charmed circle, and the argument of unfair competition will be used for all it is worth, and will be very difficult to deal with. Again, it is most important not to lose sight of the fact that the experience of the Germans is all in favour of building up very large works, and against spreading manufacturing operations over small works situated in different parts of the country.

The reason for this is obvious. In the manufacture of any substance, by-products are almost always produced which must either be recovered or used in the manufacture of other saleable products; otherwise serious loss is inevitable. It is exactly in this respect that the Germans are so efficient, and the wonderful organisation which enables them to dovetail one process into another is one of the reasons why the comparatively small works in this country find it impossible to compete with them even in the manufacture of such simple substances as salicylic acid or β-naphthol. In order that by-products may be used to the best advantage it is obviously essential that all these dovetailing operations must be carried out on the same site, so that it may not be necessary to transport the by-products from one works to another, an operation which could not fail to entail loss. Probably the best course for the new Company is either greatly to enlarge the works of

Messrs. Read Holliday and Sons, or, if it is difficult to find space for this purpose in Huddersfield, to take steps to acquire a suitable site and erect and equip works thereon, a plan which is mentioned in the explanatory statement as one of the objects of the new Company.

Let us suppose that, in the near future, a practically new works is built on a large scale, and with all the most modern appliances, and that the control of the whole works and of the different departments is placed in the hands of efficient chemical leaders with adequate staffs of chemists under their charge, and that the Company has also large and well-equipped research laboratories busily engaged in discovering new developments and improvements on existing processes; what prospect has such a works of competing successfully with the existing German organisations and of obtaining a fair share of the organic chemical industry?

In answering this important question it must again be emphasised that the German works with which the new Company must compete are enormous organisations controlling almost unlimited resources and in a most flourishing condition.

The Farbwerke, vormals Meister, Lucius, & Brüning, in Höchst, employs, for example, 350 chemists, 150 engineers and technical experts, 600 clerks, and about 10,000 workmen.* The probability of successfully competing with several organisations of this kind grouped, as they are, in combines, in order the more readily to be able to crush competitors and secure the monopoly of the industry, also depends, no doubt, to a great extent on the condition of the German chemical industries after the war. If we suppose that the German companies will continue to work with the same efficiency as before, or will rapidly regain that efficiency, I am inclined to think that we must be prepared to face the certainty that some years must elapse before we can compete successfully against organisations which have taken years to develop and bring to perfection. Many of us hold the view that, in order to prevent underselling and other unfair methods of competition, the Government ought to protect the new venture for ten years at least by placing an import duty of not less than 25 per cent. on all German dyes and other organic products. I must confess that I hold the view that this, or prohibition for a time, is the only real solution of the difficulty, and if it should be found that this course leads to slackness and rule of thumb methods, and that the works, after their period of protection, have not developed on the lines of discovery and invention, then the Government will

* Compare the letter of F. A. Mason to the *Manchester Guardian* of February 13th.

at least have the satisfaction of knowing that everything has been done on their part to establish the industry.

Failure to develop on research lines is scarcely conceivable if the works is in charge of a highly-trained chemical staff, but, on the other hand, if it gets into the power of the business man who wants an immediate return for his outlay, is not willing to wait for results, and fails to appreciate the importance of scientific control, then no tariff can avert disaster. I am sure we shall all watch the course of events with the greatest interest, and hope that the new venture may have a large measure of success, and bring back to this country at least a tithe of the prosperity which attaches to the organic chemical industry.

OBITUARY NOTICES.

FRANK BAKER.

BORN OCTOBER 20TH, 1886; DIED JANUARY 21ST, 1914.

FRANK BAKER was born at Eton, Bucks, in 1886, and died in Glasgow on the 21st January, 1914. His early training was received at the Eton Porny Elementary School, of which his father was master. After gaining Junior, Intermediate, and Senior County Scholarships, he attended the Polytechnic, Regent Street, until his matriculation with honours at London University. He spent six months at King's College, and then, in 1903, proceeded to University College, London, with an "Andrews" Scholarship. There he gained many scholarships and prizes, and finally graduated B.Sc. with First Class Honours in Chemistry.

After a year's training in research work under Sir William Ramsay, he spent a short time at the Agricultural College, Wye, and then as Science Master at a school at Widnes. Mr. Baker became a Fellow of the Chemical Society in 1907, and was a Fellow of the Institute of Chemistry. Early in 1909 he was appointed chemist in the Royal Gunpowder Factory, Waltham Abbey, which he left in 1910 to take up a post as one of the Research Chemists in the Ardeer Factory of the Nobel's Explosives Co., Ltd.

During the whole of his association with the explosives industry, Mr. Baker was occupied on the investigation of the very complicated phenomena which occur during the manufacture, storage,

and use of propulsive explosives for war purposes. His work will ultimately have a great influence on the development of this class of explosives, although he may get no direct credit for it, as it is not desirable that such information should be published.

Mr. Baker's work was mostly connected with physical and organic chemistry, and he possessed a very wide knowledge of these subjects, as well as a degree of originality which rendered him particularly efficient as a research chemist. Through his premature death, our science has lost one of its most promising young exponents.

W. RINTOUL.

CECIL REGINALD CRYMBLE.

BORN APRIL 6TH, 1885; DIED NOVEMBER 20TH, 1914.

BRIEF as it was, the career of C. R. Crymble had been marked by thoroughness and an effective activity. As a student, he had been distinguished on both the academic and social sides of University life. After graduating as B.A., he began to study medicine, but, being attracted to chemistry, he gave up his medical course and took the B.Sc. degree of the Royal University of Ireland. Thereafter in rapid succession he was appointed to the Andrews Research Studentship, the Senior Assistantship in Chemistry in the Queen's University of Belfast, and the 1851 Exhibition Research Scholarship. In addition to the Queen's University, he had studied under Sir William Ramsay and Prof. Collie at University College, London; and just before the war broke out he had been appointed to a post in the Physiology Department of the latter institution under Prof. Starling.

This career is enough to mark him out as an exceptionally able man; but he was no mere bookworm, and his activity on the social side of University life was as great as his interest in chemistry. It is safe to say that he was associated with every students' movement which took place during his University career, and in most cases he was to be found among the leaders. He was, in succession, President of the Union and of the S.R.C. of his Alma Mater, and it was largely due to his efforts that the students secured direct representation in the government of the new University at Belfast. It was no more than his due that he was selected as their first representative on the Senate.

A most successful administrator, he never forgot that what counts in a Department is not the mechanical appliances, but the human factor. His efforts were always turned towards making

the laboratory, not so much a mere place where chemistry was taught, as a sort of "home from home" in which he sought to make the shyer students perfectly at ease; and in this task he had the assistance of his own personality, for it was impossible not to feel that he became almost immediately "an old friend." Yet he never lost sight of the main object of instruction. Lucid in thinking, he was equally lucid in explanation, and he never allowed the students to realise that he was anything but one of themselves. It was often said that "One never guessed how much Mr. Crymble knew until one thought of how much he had taught one." This trait was characteristic both of his modesty and of his excellence as a teacher.

His interest in his students was by no means confined to their careers in the laboratory, however, and those who knew him well could give many instances of his kindness and generosity in matters wholly unconnected with chemistry. But eager as he was to help anyone in trouble, he was even more anxious to avoid publicity for his kindly actions, so that few recognised the full extent of his warm-heartedness in these directions.

Turning to his chemical investigations, it is interesting to note that his earliest researches, which he never published, were in the domain of biological chemistry, to which he had intended to return. His published papers dealt with absorption spectra. Some of these were published in conjunction with colleagues; but in these cases Crymble never played the part of a subordinate, for to any paper bearing his name he had contributed his full share of ideas as well as experimental work. It was characteristic of him that when he began to work independently he set himself to the investigation of the main outlines of a new field, and did not become absorbed in some minor point. His first single-handed paper marked a great advance in our knowledge of the absorption spectra of metallic ions, and the relations which he established between the valency of ions and their absorptive powers appear to be of great importance, and are likely to be of even more value when our ideas of valency changes become more clarified than they are at present.

A magnetic personality such as his cannot be described in type. One misses the inflexions of the voice, the peculiar turns of expression, the smile that flitted across his face when he recognised that the force of argument was on his side or was definitely against him. These things cannot be put down in print, and yet in the memories of those who knew him they make up a picture of his personality which cannot be displaced. His chief characteristic was constant cheerfulness and complete control of his temper. No one ever saw him more than temporarily depressed, nor did any-

one ever see him visibly angry. Yet with all this evenness of temperament he was an extraordinarily changeable personality. His mind displayed a continual change of mood, one aspect shading into another imperceptibly, so that to work with him for a day was to run through the whole gamut of character from the serious to the ludicrous.

What differentiated him from the majority of people was that he had evolved a peculiar code of chivalry of his own, to which he rigidly adhered. Place him in the same conditions twice, even though years had elapsed between the two times, and he would act in precisely the same manner on the second occasion as on the first. He had drawn certain lines for himself which no one could cross in his presence, no matter how ingeniously they endeavoured to evade the apparent conditions, and his high standard was firmly maintained.

His range of reading was of the widest. Everything interested him, and yet he never descended to the level of a mere smatterer. Anything which he took up he went into thoroughly, and he tested everything as he went along, never allowing an author to persuade him without due consideration. He had an extensive knowledge of modern literature, history, and science; he was a keen student of international politics and of military literature. In addition to this, his interests lay in art and in music.

His military career began in the Queen's University Officers' Training Corps, an institution which he had helped to found, and in which he was the first Colour-Sergeant. From this he passed to a Lieutenancy in the Special Reserve, becoming attached to the 3rd Battalion of the Royal Irish Fusiliers, in which regiment he spent a number of years. The earlier stages of the war found him in command of an infantry detachment at Dunree Fort, on Lough Swilly, where he remained for some weeks, chafing at the delay in getting to France. Finally, he was transferred to the active battalion; and then followed a period of marching, fighting, and countermarching, which he sketched so graphically in his letters.

Through it all he maintained his characteristic cheerfulness, and the tone of his letters contrasted strongly with the facts he described. For weeks he escaped untouched; then came the 20th November, and the War Office announcement, "Killed in action." His commanding officer in the report of his death spoke of him as "an exceptionally capable officer," and letters from the front have shown that he was missed, not only by his fellow-officers and the men under his immediate command, but also by the rest of the battalion to which he was attached.

A. W. S.

JOHN GUNNING MOORE DUNLOP.

BORN NOVEMBER 14TH, 1885; DIED AUGUST 27TH, 1914.

JOHN GUNNING MOORE DUNLOP was born at Holywood, near Belfast, in the year 1885. His school was Charterhouse, whence he came to Gonville and Caius College as a Scholar in 1905. He gained first-class honours in both parts of the Natural Sciences Tripos, with Chemistry as his chief subject. After taking his degree he was awarded a research studentship by the College, where he remained in residence until the outbreak of the war, devoting himself to chemical research with considerable success, as shown by frequent publications in the *Transactions* of the Society between 1909 and 1914.

During the earlier years of this period, he held the position of Junior Demonstrator in the University Chemical Laboratory, and later undertook some teaching work in College. He was one of the secretaries of the University Chemical Club, and a leading spirit in what may be called the social side of Chemistry.

He had always taken a keen interest in military work. For the last few years he had spent nearly all his vacations with the Ulster Volunteers, and he would have been as ready to fight for Ulster as he was for his country. At the outbreak of the war he volunteered at once, and was given a commission in the 2nd Royal Dublin Fusiliers, with whom he went to the front in August. After Mons he was reported missing. Hope that he might have been made prisoner was not abandoned until November 12th, when a message was received from the American Consul in Berlin stating that Dunlop was killed in action near Clary on August 27th. Three hundred and fifty men and officers of the regiment were cut off in the retreat. Only fifty succeeded in fighting their way through the enemy back to their division. Dunlop was one of those who fell.

T. B. W.

WILHELM HITTORF.

BORN MARCH 27TH, 1824; DIED NOVEMBER 28TH, 1914.

JOHANN WILHELM HITTORF was born in Bonn on March 27th, 1824. As a young man he studied in the Universities of Berlin and of his native town, where he graduated as Doctor of Philosophy in 1846 with a mathematical thesis entitled "Proprietates section-

arum conicum ex æquatione polari deductæ," which was in part published in Crelle's Journal three years later. Soon after his graduation he received a post as Privat-dozent in the Academy of Münster, which afterwards became the University of Münster. Here he devoted himself to the experimental investigation of electrolytic conduction. His *Habilitations-schrift* on the occasion of his promotion to the rank of Professor Extraordinary of Physics and Chemistry bore the title "De iontum migrationibus electrolyticis," and formed the first part of those classical researches on the migration of the ions, which are inseparably associated with his name.

Daniell and Miller had criticised the idea, prevalent at that time, that the equivalence of the substances liberated at the two electrodes on electrolysis is due to the oppositely charged ions moving at the same rate, and had pointed out that this hypothesis of the equivalent transfer of the ions "although generally received, is itself destitute of foundation," basing their criticism on the results which they had obtained by analysing the contents on the two sides of a porous diaphragm placed between the electrodes of an electrolytic cell. Hittorf used the same method in principle, and carried out the work with the utmost patience and experimental skill, so as to establish not only the fact of the non-equivalent transport of the ions, but to measure their transport numbers, that is, the proportion of the total electricity carried by the anion and cation respectively, from which the relative velocities of migration of the ions could be calculated.

Hittorf showed that within wide limits the transport numbers were independent of the current strength, and the influence of temperature he also ascertained to be small. Concentration, however, was found to have a considerable effect on the transport numbers, although in every case these numbers tended to a constant value at extreme dilution, and in the case of ammonium and potassium chlorides were nearly independent of the dilution.

Besides leading to these results with simple salts, the investigation of the change of concentration at the electrodes on electrolysis led Hittorf to definite deductions as to the existence or non-existence of double salts in solution. Solutions such as those of potassium magnesium sulphate behaved as mere mixtures of potassium sulphate and magnesium sulphate, each single salt acting as if it were independent of the other. On the other hand, solutions of potassium silver cyanide, sodium platinum chloride, and potassium ferrocyanide showed the same phenomena as those of single salts, the alkali metal being the sole cation, and the heavy metal appearing only as a component of the anion.

Solutions of the double iodide of potassium and cadmium were shown to be intermediate in their behaviour between these two classes. In concentrated solutions potassium was practically the only cation; in dilute solutions cadmium as well as potassium appeared as a cation, the complex salt, K_2CdI_4, thus splitting up on dilution into two simple salts, KI and CdI_2.

The chlorides and iodides of zinc and cadmium were found by Hittorf to exhibit interesting phenomena. Cadmium iodide, for example, showed an accumulation of iodine at the anode greater than was equivalent to the deposition of cadmium on the cathode. Even on the supposition that the cadmium ion was stationary, such an excess could not be accounted for if the ions of cadmium iodide were Cd and 2I, as had been supposed. Hittorf assumed that the molecule of dissolved cadmium iodide was a multiple of CdI_2, say, Cd_3I_6, and that the cation and anion respectively were Cd and Cd_2I_6, cadmium thus moving towards the anode as well as towards the cathode. These phenomena were only noted in concentrated solutions, disappearing gradually as more dilute solutions were investigated.

By such experiments Hittorf laid the foundation of the exact investigation of complex salts in solution. He showed, too, that in solutions of stannic chloride the electrolyte was hydrochloric acid, and that the tin played no part in the transport of electricity, whereby he established the fact that in solution stannic chloride is completely hydrolysed.

His general ideas on electrolysis were of much interest. Besides the celebrated statement "Electrolytes are salts," the following passage from one of his later papers may be quoted: "The electric phenomena which I have observed show conclusively that the heat of formation of compounds and the firmness of union of their components do not stand in the relation of cause to effect. This conception, adopted by nearly all chemists, is completely contradicted by the phenomena of electrolysis. Here the two things appear apart and mutually independent. The heat of formation shows itself as electromotive force, and the mobility of the components appears in the electric resistance of the fluid compound." The capacity for reaction is connected, not with heat evolution, but with conductivity.

Notwithstanding the accuracy and importance of Hittorf's researches on electrolysis, they were for long unrecognised. He had become ordinary Professor of Physics and Chemistry in Münster in 1856 (and Professor of Physics alone when the chair was divided in 1879), but it was only in 1880, twenty years after the completion of his main work, that he received his first scientific

honour, namely, the corresponding membership of the Göttingen Academy of Sciences.

Meanwhile he had been busy in other directions. In conjunction with Plücker (1865) he investigated the spectra of ignited gases and vapours in Geissler tubes, the investigation leading to the conclusion that one element could have more than one spectrum. At low temperatures and with feeble currents, band spectra were observed; at higher temperatures and with heavier discharges, line spectra; and at still higher temperatures and pressures, continuous spectra. He also discovered the form of phosphorus known as "metallic" phosphorus, and showed that the vapour from red phosphorus on rapid cooling yielded yellow phosphorus.

His association with Plücker led him in 1869 to an investigation of cathode rays, discovered by the former ten years previously, in which he showed that cathode rays cast a definite shadow of a solid body placed in their path, the shadow depending only on the form of the solid, and not on its being opaque or transparent, a conductor or a non-conductor. Between 1874 and 1884 he turned his attention to electric currents in flames, to the cathode fall of potential, and to the variation of electric force and of the temperature along a discharge-tube. His striking experiment of the difficulty of producing short sparks dates from the end of this period.

In 1890, at the age of sixty-six, he retired from active teaching, owing to ill-health, and the title of Professor Emeritus was conferred upon him. This might well have marked the termination of his scientific career, but with a wonderful recovery of energy he entered in 1894 on another decade of scientific labour, the results of which bear comparison with his earlier work. He investigated the abnormal electromotive behaviour of chromium, and in connexion with this the general subject of the passivity of metals. The "hydrates" of platinum and gold chlorides, $PtCl_4,H_2O$ and $AuCl_3,H_2O$, were proved by him to be complex acids, $H_2{\cdot}PtCl_4O''$ and $H_2{\cdot}AuCl_3O''$ respectively, the heavy metal in each case moving with chlorine to the anode during electrolysis. As further experimental evidence of this view he prepared the silver salts $Ag_2{\cdot}PtCl_4O''$ and $Ag_2{\cdot}AuCl_3O''$. His last series of researches returned to the subject which first occupied his scientific attention, namely, the measurement of transport numbers. He showed that some diaphragms in the electrolytic cell have a considerable influence on transport numbers, whilst others prevent mixing without introducing sensible errors. He showed further that some solutions pass as a whole through animal membranes during electrolysis, whereas others separate into more or less concentrated

solutions on the two sides of the membrane, owing to a difference in the rate of transference of solute and solvent. Some excessively accurate determinations of transport numbers with the aid of diaphragms bring his long record to a fitting close in 1903, his scientific activity having extended over fifty years.

For ten years more Hittorf lived on quietly in Münster, where he died on November 28th, 1914, in his ninety-first year.

Heinrich Goldschmidt, who visited him on his ninetieth birthday, relates that, although somewhat oppressed by years, the veteran retained an excellent memory and took an active interest in general affairs. Hittorf lived practically his whole life in the peaceful Westphalian town. He never married, and travelled but little, a single visit to England being his longest journey. For a long period of his life he keenly felt the neglect with which his scientific work had been treated, but in his later years honour came to him in plenty.

He was elected a Foreign Member of the Society in 1908, and the disappearance of his name from the roll marks the passing of one more of the founders on whose work modern physical chemistry is built.

J. W.

EDWARD RILEY.

BORN 1831; DIED SEPTEMBER 12TH, 1914.

EDWARD RILEY was born in 1831, and educated at King's College School, London, and at the Putney Civil Engineering College. He then studied under Dr. Lyon Playfair (afterwards Lord Playfair) at the laboratory of the Board of Health, and subsequently assisted him in the laboratory in Jermyn Street, where he remained until 1853. On the recommendation of Sir Henry de la Beche, President of the Geological Survey of England, he was appointed chemist to the Dowlais Iron Works in South Wales. Mr. Riley was intimately associated with the early experiments in connexion with the Bessemer process of steel manufacture. In 1859 he resigned his position at Dowlais, and started in private practice as a consulting and analytical chemist in London, and it was there that he did much analytical work for Sir Henry Bessemer during the time he was developing the Bessemer process.

Mr. Riley's name has always been associated with titanium and titaniferous minerals. He carried out a very exhaustive investigation as to the value of titaniferous iron-ore deposits of Norway, and demonstrated that almost all grey pig-iron made in blast

furnaces contained some titanium, but that this element was not present when the iron was white in fracture. For two or three years Riley resided at Leeds, experimenting with titaniferous ores, but finally abandoned his experiments. During his residence in Leeds he married, and soon afterwards returned to London and continued his practice at Kensington.

In 1869 he removed his laboratory to Finsbury Square, where the firm, under the style of Edward Riley and Harbord, still continue to practice as consulting metallurgists and analytical chemists. At that period there were very few authorities in Great Britain whose analyses of material required for the manufacture of iron and steel were recognised; indeed, forty years ago Mr. Riley in London, Mr. John Pattinson in Newcastle, and Mr. R. R. Tatlock in Glasgow were looked upon as of equal authority .

Riley, together with other chemists during the development of the Thomas and Gilchrist Basic Bessemer process, at an early date were convinced that the preparation of the basic material for lining the converters was not based on scientific principles. The inventors prescribed mixing the calcined and shrunk dolomite with an aqueous solution of sodium silicate, the water of which, of course, slaked the lime and caused the lining to disintegrate. Riley, therefore, patented the use of hydrocarbons, such as petroleum, tar, etc., as a substitute for aqueous sodium silicate. He also patented the application of bricks made by mixing slaked lime and petroleum for lining converters. On trial it was found that the bricks made by Mr. Riley's process disintegrated when strongly heated, and were useless as a lining for converters. The lining which did stand was made by mixing shrunk dolomite with boiled coal-tar, and it is this which is universally used at the present time. Mr. Riley was given a share in the Basic Patents, and in this way became associated with the basic or Thomas and Gilchrist process. Eventually, with others, he started the North Eastern Steel Co., Ltd., and Messrs. Hickman, Ltd., and became a director of both companies. He read many papers before the Chemical Society and the Iron and Steel Institute embodying methods of analysis, some of which are used to-day, but many, of course, as one would expect, have been improved since that time. Mr. Riley maintained the full enjoyment of his faculties up to the time of his death, which occurred when he had reached the age of eighty-three years. A few years ago he retired from active work, and took into partnership Mr. F. W. Harbord. He was awarded the Bessemer medal at the meeting of the Iron and Steel Institute last year. He had resided at Marlow, on the River Thames, for twenty-six years, and although unable to take any active part in professional work was keenly

interested in all matters connected with the metallurgy of iron and steel up to the time of his death.

J. E. S.

JOSEPH WILLIAM THOMAS.

BORN MARCH 9TH, 1846; DIED MARCH 3RD, 1914.

JOSEPH WILLIAM THOMAS will be best remembered among chemists for his researches on the gases of coals. Born at Llwyn-y-grant, Penylan, near Cardiff, in 1846, he was educated at private schools at Cardiff and at Bath. After leaving school he for some time assisted his father, the late Mr. Daniel Thomas, the well-known contractor, who carried out many large undertakings in Cardiff and its neighbourhood, including the West Bude Docks, the bridge over the Taff, and the Cardiff-Penarth roadway, besides important railway contracts. At this time J. W. Thomas was also much interested in literary work, and wrote, and produced in London, several successful plays. Even as a boy Mr. Thomas had been attracted to chemistry, and in his schooldays had fitted up a laboratory at home; as time went on his interest in the subject increased, and finally he decided to study chemistry at the Royal College of Science, South Kensington. In these laboratories he worked for some years, and it was during this period that, under the guidance and advice of Prof., afterwards Sir Edward, Frankland, he carried out the laborious series of gas-analyses in connexion with his work on the gases of coal. In addition to laboratory work this research entailed a very large amount of practical work underground, for during the course of it Thomas collected samples of gas from every important colliery in South Wales. The scope of the work is perhaps best indicated by the titles of three memoirs that he contributed to our *Transactions*: "On the Gases enclosed in Coals from the South Wales Basin, and the Gases evolved by Blowers and by boring into the Coal itself" (this Journal, 1875, **28**, 793); "On the Gases enclosed in Cannel Coals and Jet" (*ibid.*, 1876, ii, 144); "On the Gases enclosed in Lignite Coal and Mineral Resin from Bovey Heathfield, Devonshire" (*ibid.*, 1877, ii, 806). A good summary of the methods employed and results obtained will be found in the third supplement to Watts's "Dictionary of Chemistry."

Later he reviewed the whole subject of the gases in coal in a book he published in 1878, "Coal-mine Gases and Ventilation," which is still regarded as a standard work on the subject.

Mr. Thomas's further contributions to chemical literature were all more or less directly connected with gas analysis. He described a modified form of the Frankland-McLeod apparatus for gas analysis, which contained several ingenious devices to facilitate working and to obviate leakage or fracture (T., 1879, **35**, 213), and several of the absorption methods in gas-analysis were investigated by him. Two other papers deal with reactions to which his attention had been called when using certain absorption methods. The more important is an investigation of the action of gaseous hydrogen chloride on solutions of various metallic salts (T., 1878, **33**, 367). Thomas was a most careful worker; those who were in the South Kensington laboratories at that time have a vivid remembrance of the ardour with which he attacked the problem before him, and of the pains he took to assure that his results should be as accurate as possible.

After leaving South Kensington, Thomas established a laboratory at Cardiff, where he worked for many years. He was the first public analyst appointed for Cardiff, for the County of Glamorgan, and for the Borough of Newport. Mr. Thomas spent the latter part of his life in endeavouring to instil into the minds of those responsible for the design of public buildings the necessity of grasping the fundamental principles of successful warming and ventilation. In 1903 he published a treatise on "The Prevailing Errors in the Ventilation of Churches, Halls, Schools, and other Public Buildings," followed in 1906 by a more ambitious work on the "Ventilation, Heating, and Lighting of Dwellings." Reference may also here be made to two other books that he wrote: "Spiritual Law in the Natural World" (1894) and "Intuitive Suggestion, or a New Theory of the Evolution of Mind" (1901).

In his native district Mr. Thomas was well known as a popular lecturer on scientific subjects, especially natural history, to which he gave much time. By way of recreation he made a very large collection of British moths and butterflies; this, it is understood, he has left to the new National Museum of Wales. He was an excellent draughtsman; his botanical drawings are conspicuous for minute detail and microscopic accuracy—they are treasured by those who are so fortunate as to possess them.

Mr. Thomas died suddenly in London on March 3rd, 1914, at the age of sixty-eight.

JOHN GREENAWAY.

ROBERT WILLIAMSON.

BORN SEPTEMBER 21ST, 1853; DIED SEPTEMBER 24TH, 1914.

ROBERT WILLIAMSON was born in North Shields on September 21st, 1853, and was the fourth son of the late George Williamson, Esq. He was educated first at a local school in North Shields, and subsequently entered the High School at Edinburgh, where he remained for six years, and it was here that he showed his first taste for science, and decided to adopt chemistry as a career. His ability was indeed so marked that soon after leaving school he was accepted as assistant to the late John Pattinson, who practised as a public analyst, and in those days had a high reputation throughout the North of England.

Feeling, however, the need for further study, and desiring rather to become a technical chemist than a professional analyst, he did not remain long in this position, but proceeded to the Royal College of Chemistry, then under the direction of Prof., afterwards Sir Edward, Frankland. His progress here was rapid, and at the conclusion of the course he was at once recommended as suitable for the post then vacant of research assistant to the late Sir William, then Mr. W. H., Perkin. At this period the colour factory of Perkin and Sons at Greenford Green was in its zenith, and although Williamson was not employed actually in the works, being indeed placed in the external laboratory in the Greenford Road, he found his work peculiarly interesting. There is unfortunately no actual record of his concern with any special investigation carried on at this time, but there can be little doubt that in addition to the examination of factory products, he took part in work on anthrapurpurin and anthraflavic acid, both of which were discovered at or about that period.

Williamson was naturally disappointed when in 1874 the Greenford factory passed into the hands of Messrs. Brooke, Simpson, and Spiller, but, on the other hand, although he could have obtained service with the new firm he did not do so, in the hope that he might still participate in colour chemistry problems similar to those in which he had formerly been engaged.

To a certain extent his anticipations were realised, and although he was always proud of his connexion with the "Perkin reaction" which shortly afterwards emanated from the new Sudbury laboratory, by preference he would rather have been entirely engaged in the study of dyestuffs.

Feeling now that his apprenticeship must cease, he accepted an

engagement as chemist in the City laboratory of Messrs. Nelson, Dale and Co., the well-known gelatin manufacturers, and it is there no doubt that he acquired a taste for this subject which proved of service to him in later years.

In the meantime the factory of Perkin and Sons, which had been purchased by Messrs. Brooke, Simpson, and Spiller, passed into the hands of Messrs. Burt, Boulton, and Haywood (now the British Alizarin Co.), who removed the manufacture from Greenford to a site at Silvertown adjacent to their tar distillery. An opportunity of entering this factory was readily accepted by Williamson, and here after a short period of laboratory work he was placed in charge of the anthraquinone process, Mr. Thos. Royle being general manager.

The tenure of the alizarin patents was now approaching conclusion, and attempts were made by the manufacturers to ensure if possible their monopoly for a further period. At this juncture the late Mr. Josiah Hardman, on behalf of his firm, Messrs. Hardman and Co. (now Hardman and Holdens), of Miles Platting, Manchester, decided to start the manufacture of alizarin, and having safeguarded himself, by entering into satisfactory contracts, engaged Williamson to erect and manage the factory.

That Williamson readily undertook these duties speaks highly for his courage and ability, for even at the present time the preparation of alizarin on the large scale is one of the most complex technical processes.

A severe handicap he had to face was the quality of the anthracene available in the district, for this, derived from Lancashire tar, as was well known, is far inferior to that produced in Newcastle and the district. This arises from the fact that in the Lancashire variety, in addition to traces of paraffin wax, a considerable quantity of β-methylanthracene is present, the alizarin derived from this possessing inferior dyeing virtues to that obtainable from anthracene itself. These difficulties at that time, new to Williamson, were only overcome by exhaustive experiment, but he was, however, able when the factory he had designed was nearing completion, to feel certain he could produce a satisfactory material, an assumption he later fully justified.

Of the factory he erected for Messrs. Hardman and Holdens Williamson was exceedingly proud, and justly so, for it was universally acknowledged by those permitted to inspect it, to be a model from which the colour works in this country and elsewhere might well take an example.

The manufacture continued there for several years, and as the result of its working there is no doubt that the firm reaped sub-

stantial benefit. More latterly, however, the fall in price rendered its continuation without additional plant extension hardly worth while, and the margin even then being small, the factory was eventually reconverted and employed, as is still the case, for other purposes.

About four years before this occurred, Williamson removed to Middlesborough, and was engaged in the manufacture of alizarin at the works of Messrs. Sadler and Co., who had entered the field at a date later than Messrs. Hardman and Holdens.

Subsequently he returned to Newcastle, where he eventually settled and started, in conjunction with Mr. Walter Corder under the name of Williamson and Corder, a gelatin factory, which is carried on at the present time, and is highly successful.

Although Williamson could without doubt have done well as a pure chemist, as the research he published ("On Some Metallic Derivatives of Coumarin," *J. Chem. Soc.*, 1875, **28**, 850) while at Sudbury indicates, he was at heart a technologist, and appeared never to be so happy as when surrounded by the hum of factory life.

As the writer knew him, he possessed great energy, was calm in the face of unexpected difficulty, and courageous to a degree when occasion required.

He possessed the happy gift, so essential to a works manager, of controlling men, with whom, although firm, he was always lenient and on terms of good fellowship.

Elected to the Chemical Society on December 24th, 1874, he became during his stay in the south, a well known figure at the Ordinary Meetings, and later when this attendance was no longer possible he interested himself in the scientific societies of those other towns in which he for the time resided. More recently he became absorbed in his own business, and was rarely present in scientific circles. He was one of the earlier Fellows of the Institute of Chemistry, which he joined in 1878.

After a period of ill-health, he went to Scarborough in the hope of deriving benefit from the change, but unfortunately this did not prove to be the case, and he died suddenly on September 24th, 1914, at the age of sixty-one.

Williamson was a Conservative in politics, a member of the Church of England, and was unmarried.

By his death the last of the little group of chemists who were connected with Sir William Perkin's colour factory at Greenford Green has now passed away.

WILLIAM JAMES SELL.

BORN OCTOBER 14TH, 1847; DIED MARCH 7TH, 1915.

WILLIAM JAMES SELL was born at Cambridge in 1847, and made his way in life by his own mother wit and his steady, single-minded character. He began to learn chemistry early, for he was not quite fifteen when, on the recommendation of the master of the elementary school which he attended, he was employed at the chemical laboratory of St. John's College, at that time the only place in Cambridge where practical instruction in chemistry was given. He made good use of his opportunities there, and in 1866, when the University supplied some rooms for a students' laboratory, he was appointed attendant, and had charge of the apparatus and assisted the Professor of Chemistry in the experiments shown at his lectures. He soon became an expert manipulator, and at the same time acquired a sound knowledge of theoretical chemistry. His post was poorly paid, but his skill, and interest in his work, contributed largely to the development of the laboratory, which at first was of a very makeshift sort. He not only assisted the professor, but gave efficient help to many of the students who had no training in observation and no notion of how to make an experiment.

He married when he was twenty-two years old, and a few years later he entered the University as a member of Christ's College. As a boy he had learnt neither Latin nor Greek, and some knowledge of both was essential for obtaining any degree at Cambridge. He set to work, with quiet resolution, at such times as his duties at the laboratory allowed, to acquire this knowledge, and successfully passed the preliminary examinations, and was free to take the B.A. Degree with honours in Natural Science. This he did in 1876, obtaining a First Class for Chemistry. He now took up teaching, exchanged his post at the laboratory for that of Demonstrator, an office little better paid, but which allowed him to increase his income by taking private pupils. A year or two later he succeeded to the office of Principal Demonstrator, and held it to the end of his life. All through this time he contributed much to the healthy life of the place. He set an example by always doing his best, without a trace of ostentation, to keep going forward. Science was expanding rapidly, and it taxed the energies of the staff to keep the laboratory and its teaching equally advancing. Sell took his full share of the task, and all his colleagues acknowledge how faithfully and ungrudgingly his help was given. More lectures were required, not only because the number of students

increased and had to be classified according to their attainments, but because new discoveries demanded more lectures for their elucidation. Hence Sell became quite as much a lecturer as a demonstrator.

In 1887 the new chemical laboratory of the University was opened, and gave greater facilities in every way. It was after this that most of Sell's original work was done. Hitherto the exigencies of maintaining his family prevented him from undertaking unremunerative work, but now his income was somewhat larger, and he was able to get the assistance of some of the advanced students in carrying out researches which involved prolonged experimental work. He had already published in 1882 (*Proc. Roy. Soc.*) an account of a series of salts of a base containing chromium and carbamide, which was much further extended in another paper published in 1888; much more important were a long series of investigations on pyridine derivatives, of which the records appear in the *Transactions* of the Chemical Society at intervals from 1892 to 1912. They originated in a research, carried out in conjunction with T. H. Easterfield, on the action of acetyl chloride on citric acid, which resulted in the formation of acetylcitric anhydride. Among other transformations, this compound, on treatment with ammonia, was converted into citrazinic acid. The authors were thus led to investigate citrazinic acid, and in the course of an examination of its behaviour towards nitrous acid they discovered some very remarkable derivatives, of which, in spite of further work, the nature is still not completely elucidated. Together with F. W. Dootson, he then studied the action of phosphorus pentachloride on citrazinic acid, and found that this reagent brought about, not only the replacement of the hydroxyl groups, but also that of hydrogen by chlorine, leading finally to the production of pentachloropyridine. They were thus led to examine the action of phosphorus pentachloride on pyridine itself, and obtained a complex mixture of chloro-derivatives, from which they succeeded in isolating eight pure compounds, a dichloropyridine, three trichloropyridines, the three possible tetrachloropyridines, and pentachloropyridine. By the action of chlorine on pyridine hydrochloride they further obtained, along with a di-, a tetra-, and penta-chloropyridine, some very remarkable dipyridyl compounds. Sell also examined the action of chlorine on α-picoline in a similar way. His further work was devoted principally to the determination of the constitution of the numerous chloropyridines which he had discovered, and to the examination of their characteristic chemical properties. In this he was very successful, and he was able to determine the orientation of the chlorine in most of the compounds

which he described, largely using for that purpose the chloroamino-compounds which he obtained by treating the chloropyridines with ammonia. A contribution also to inorganic chemistry in the preparation of colloidal solutions of ferric, aluminic, and chromic phosphates by dialysis of their solutions with excess of ammonium phosphate deserves to be mentioned. All is very sound and thorough work, for Sell had the instinct of an honest searcher for truth, and would leave nothing to chance which could be assured by taking enough trouble.

His work in the chemical laboratory, although carried on so long and so steadily for the advancement of science and the credit of the University, never received at Cambridge the particular recognition it deserved. He had been elected a Fellow of the Royal Society in 1900, and took the degree of Sc.D. at Cambridge in 1906. His friends were much disappointed when their effort to get him made a "Reader" in Chemistry failed. Sell himself was so averse from putting himself forward that it was little known outside the laboratory what valuable service he was rendering, and the University at large did not seem to see that his claim to a Readership was stronger than those of claimants in other departments which could not all be met at once. Perhaps some did not wish to see, for the devotees of literature are jealous of the overwhelming growth of physical science which seems to absorb so much of the strength of the University, both mental and material. Sell had to be content with the honour of a University Lectureship with a stipend of £50 a year, and did not grumble.

By his death Science has lost a faithful follower, the staff of the University laboratory a willing and unassuming fellow-worker, and the students a sound, painstaking, and very kind instructor.

G. D. L.

LXI.—*Mangostin: a Crystalline Substance Allied to the Resins.*

By John Robertshaw Hill.

Mangostin occurs in all parts of the mangosteen tree (*Garcinia mangostana*), which is cultivated in the Tropics for its fruit. The latter is enclosed in a thick, dark red skin, which contains in the dry state about 10 per cent. of resin. The resin can be separated into a crystalline portion, which is mangostin, and a non-crystalline portion approximately equal in amount.

The fact that mangostin is crystalline and can be obtained in a

pure state induced me to undertake an investigation with the object of ascertaining its formula, and, if possible, its constitution. A knowledge of these should be of value in dealing with the resins which are uncrystallisable mixtures, and from which definite results can only be obtained with difficulty.

In 1865 Schmid (*Annalen*, 1865, **93**, 83) isolated this substance, and gave it the name mangostin. He ascribed to it the formula $C_{20}H_{22}O_5$, based only on the results of analysis. Since Schmid's work nothing more appears to have been published on the subject, and the above formula, which is now shown to be incorrect, has been accepted up to the present time.

Mangostin crystallises in small, flat, pale yellow needles. It is odourless, tasteless, and insoluble in water. It melts to a clear liquid, which on cooling forms a brittle, transparent solid. Mangostin resembles the naturally occurring resins in the following respects: it burns with a luminous, smoky flame; on rubbing between two surfaces, such as the fingers, it causes great friction and vibration owing to a certain stickiness typical of the natural resins; it occurs in the resin ducts of the plant, together with other resinous material. It is also soluble in alkalis, ethyl alcohol, ethyl ether, and many other solvents.

The results of analyses and molecular-weight determinations indicate that mangostin has the formula $C_{23}H_{24}O_6$.

Experimental.

Considerable quantities of mangosteen fruit skins were dried and powdered. The powder was extracted several times with 94 per cent. alcohol in percolators, and the alcoholic extract distilled on a water-bath under diminished pressure until most of the alcohol was removed. The syrupy residue was then shaken with water, when all sugars and soluble matter were removed, leaving the resin undissolved. This was washed by decantation, dried, and dissolved in warm benzene with the addition of a small quantity of ether. The solution was filtered, and after some time crystals of mangostin were deposited, which were collected and washed with a little benzene. The mangostin was then further purified by many recrystallisations from alcohol with the addition of a small quantity of water until the melting point became constant at 181—182° (uncorr.):

0·2168 gave 0·5535 CO_2 and 0·1173 H_2O. C = 69·61; H = 6·06.
0·2196 „ 0·5604 CO_2 „ 0·1219 H_2O. C = 69·60; H = 6·21.
$C_{23}H_{24}O_6$ requires C = 69·67; H = 6·10 per cent.

Mangostin is readily soluble in ethyl alcohol, ethyl ether, acetone, ethyl acetate, or amyl alcohol, more sparingly so in benzene, chloro-

form, ethylene dibromide, or acetic acid, and is insoluble in water or light petroleum. It is insoluble in alkali carbonates, but forms a red solution in alkali hydroxides, and is reprecipitated by carbon dioxide and acids; in these respects it behaves as a phenol.

On adding ferric chloride to an alcoholic solution of mangostin a greenish-brown coloration is produced, which is discharged by hydrochloric acid. Mangostin reacts with bromine in acetic acid and with concentrated sulphuric acid, but definite products were not isolated. Warm nitric acid oxidises mangostin with the formation of oxalic acid and other products. Attempts were made to obtain acetyl and benzoyl derivatives; the former was unstable, and could not be purified, and the benzoyl derivative could not be induced to crystallise. A methyl derivative was, however, readily obtained.

The molecular weight of mangostin was determined by the cryoscopic method, the solvents employed being phenol and methyl oxalate:

0·8609, in 18·95 phenol, gave $\Delta = 0·80°$. M.W. = 408·6.
0·4767 „ 16·65 „ „ $\Delta = 0·52°$. M.W. = 396·3.
0·8483 „ 16·65 „ „ $\Delta = 0·935°$. M.W. = 392·3.

$C_{23}H_{24}O_6$ requires M.W. = 396.

In order to confirm these results, methyl oxalate was employed as a solvent. Its molecular depression was determined by means of *p*-benzoquinone and of nitrobenzyl chloride, the mean value being 45·5°:

1·2260, in 20·705 methyl oxalate, gave $\Delta = 0·67°$. M.W. = 402·1.

Determination of Methoxyl.

Zeisel's method gave the following results:

0·2013 gave 0·1073 AgI. OMe = 7·04.
0·2269 „ 0·1221 AgI. OMe = 7·10.

$C_{22}H_{21}O_5(OMe)$ requires OMe = 7·83 per cent.

Determination of Hydroxyl.

The number of hydroxyl groups could not be determined by the action of benzoyl or acetyl chloride as the product could not be purified. It was found, however, that mangostin could be readily methylated, and this gave a means of determining the number of hydroxyl groups present. Details of the preparation and properties of the methyl derivative are described below. It was obtained in a high state of purity, and a determination of the methoxyl groups present was performed by Zeisel's method with the following results:

0·2613 gave 0·4493 AgI. OMe = 22·68.
0·2000 „ 0·3148 AgI. OMe = 20·77.
$C_{22}H_{19}O_3(OMe)_3$ requires OMe = 21·93 per cent.

The methyl derivative therefore contains three methoxyl groups, two of which have been introduced by methylation; the results of the analysis of this compound given below also prove that two methyl groups have been introduced. Mangostin therefore contains two hydroxyl groups.

This result was confirmed by titration:

Thirty c.c. of *N*/10-potassium hydroxide were thoroughly stirred with an excess of mangostin. The solution was then filtered, and the filter paper washed once with distilled water. To the clear filtrate 31 c.c. of *N*/10-sulphuric acid were added, precipitating the mangostin. The precipitate was collected, washed several times, and dried; it was then extracted with alcohol, and the solution was evaporated to dryness in a tared basin. The weight of mangostin obtained in this way was 0·5711 gram. The excess of acid in the aqueous filtrate was titrated with *N*/10-potassium hydroxide and required 1·4 c.c.; thus 0·5711 gram of mangostin was dissolved by 29·6 c.c. of *N*/10-potassium hydroxide or 396 grams of mangostin, combined with 114·9 grams, or practically 2 gram-molecules of potassium hydroxide. Mangostin therefore contains two hydroxyl groups, both of which are phenolic.

Thus three of the six oxygen atoms in mangostin have been accounted for. Carbonyl groups could not be detected, but this does not preclude the possibility of a ketonic group being present in a closed chain.

Various means of decomposing the molecule of mangostin were adopted in order to throw further light on its constitution. Several oxidising agents were employed. Hydrogen peroxide appeared to have no action, and chromic acid did not give any product that could be separated. Warm nitric acid produced oxalic acid readily, even when largely diluted with acetic acid, and other products which were not identified. Concentrated solutions of potassium permanganate oxidised solid mangostin with the formation of oxalic acid, but the substances formed by the action of less concentrated solutions could not be identified.

Fusion with potassium hydroxide gave indications of being the most satisfactory method of decomposing the mangostin molecule. The fusion was carried out at about 250°, and 5 parts of potassium hydroxide were employed for one part of mangostin. The vapours given off during the fusion were condensed, and a small quantity of an oily liquid with the odour of amyl alcohol was obtained. The aqueous solution of the fusion was acidified

and extracted with ether, and the ethereal extract was shaken several times with sodium hydrogen carbonate solution to separate the acids. The last solution was again acidified with sulphuric acid and the liberated acids were extracted with ether. After removing the ether by distillation, the acid residue was distilled in a current of steam, the distillate being treated with an excess of lime. The excess of lime was removed by passing carbon dioxide, boiling, and filtering. By concentrating the filtrate, crystals of calcium benzoate were obtained.

In a repetition of the fusion, the aqueous solution was saturated with carbon dioxide and extracted with ether, and subsequently with alcohol, which did not mix with the solution. The alcoholic extract, containing potassium salts, was evaporated, acidified with sulphuric acid, and distilled in a current of steam. The distillate was collected in an excess of barium hydroxide, and, after removal of the excess with carbon dioxide, was evaporated to a syrup, but the barium salts did not crystallise. The sodium salts were then prepared by the addition of sodium sulphate, and, after being partly purified, were converted into the silver salts. The crystalline precipitate was collected and recrystallised, when it was found that it could be readily separated into a soluble and an almost insoluble portion. Each of these salts was purified separately. When a small portion of the insoluble salt was heated with sulphuric acid a liquid distillate was obtained, which had a very penetrating odour strongly resembling that of butyric acid. A determination of the equivalent weight of the acid by estimating the amount of silver in the silver salt (Found, equiv. wt. = 101·6) indicated that the salt was silver valerate (equiv. wt. of valeric acid = 102); the presence of an amyl group in mangostin, indicated by the production of amyl alcohol during the fusion with potassium hydroxide, is thus confirmed.

The more readily soluble salt which was obtained in larger quantity was found to be silver acetate.

Thus the products obtained by the fusion with potassium hydroxide were amyl alcohol and benzoic acid in one case; and amyl alcohol, and acetic and valeric acids in the other case.

Dimethyl Mangostin.

This derivative was readily obtained as mentioned above by the methylation of mangostin. The latter was dissolved in dilute potassium hydroxide, and an excess of methyl sulphate added to the clear solution. On shaking, the methyl derivative rapidly separated with evolution of heat; after some time it was collected, washed, dried, and purified by repeated crystallisation from

alcohol. It crystallised in long, slender, silky needles, which were pale yellow when viewed in bulk, and melted at 123° (uncorr.). It is very sparingly soluble in cold, more readily so in hot alcohol, and readily soluble in ether:

0·2002 gave 0·5198 CO_2 and 0·1195 H_2O. C = 70·83; H = 6·68.
0·2020 „ 0·5235 CO_2 „ 0·1218 H_2O. C = 70·67; H = 6·74.
$C_{25}H_{28}O_6$ requires C = 70·72; H = 6·65 per cent.

The estimation of methoxyl in this derivative is recorded above. It contains three methoxyl groups, and is therefore a dimethyl derivative of mangostin.

Derivative obtained by the Action of Hydriodic Acid on Mangostin.

In the estimation of methoxyl by Zeisel's method it was noticed that a crystalline substance separated from the liquid. A larger quantity of mangostin was therefore boiled with hydriodic acid under a reflux condenser for about twelve hours. After cooling, the solid portion was washed and dried. On crystallising from alcohol, long, silky needles separated, having a pale yellow colour in bulk. After several recrystallisations the melting point became constant at 180—181° (uncorr.).

This substance is dimorphous. When the slender needles were kept in the mother liquor overnight they were frequently converted completely into short rhombs, especially if some of the latter were already present in the liquid. The phenomenon was not investigated crystallographically. Both varieties had the same melting point, chemical properties, and composition.

An alcoholic solution of this derivative gave a deep green coloration with ferric chloride. It is soluble in aqueous potassium hydroxide, very sparingly in the cold, but more so by heating or by the addition of a small quantity of alcohol. The substance is insoluble in sodium carbonate solution, hot or cold:

0·2062 gave 0·5274 CO_2 and 0·1109 H_2O. C = 69·75; H = 6·02.
0·4573, in 19·452 phenol, gave $\Delta = 0·43°$. M.W. = 393·6.
1·0412 „ 20·224 „ „ $\Delta = 0·90°$. M.W. = 412·0.
$C_{22}H_{22}O_6$ requires C = 69·11; H = 5·81 per cent. M.W. = 382.

A *methyl* derivative was readily obtained by dissolving the substance in potassium hydroxide with the addition of a little alcohol, adding an excess of methyl sulphate, and shaking, when the methyl derivative separated in very pale yellow crystals. It is very sparingly soluble in ether or cold alcohol, but crystallises well from a mixture of alcohol and chloroform, and melts at 216° (uncorr.). The fact that this methyl derivative is different from dimethyl

mangostin shows that the hydriodic acid has had some further action on mangostin in addition to the removal of the methyl group. This is also indicated by the results of combustion.

The *acetyl* derivative was obtained by heating the substance with acetic anhydride and sodium acetate. After crystallisation from benzene, in which it is sparingly soluble, it melts at 218—219° (uncorr.). The number of acetyl groups introduced was estimated by hydrolysis with alcoholic potassium hydroxide for eight hours, then acidifying, and distilling off the acetic acid. The distillate was titrated with $N/10$-potassium hydroxide:

1·4805 acetyl derivative required 33·7 c.c. $N/10$-KOH. Ac = 9·79.

$C_{22}H_{21}O_6Ac$ requires Ac = 10·13 per cent.

The results show that only one acetyl group has been introduced, and therefore that the compound resulting from the action of hydriodic acid on mangostin contains only one hydroxyl group.

Summary.

Mangostin occurs in *Garcinia mangostana* or the mangosteen tree of the Tropics. It is crystalline, but in other respects resembles the natural resins.

Its molecular formula is $C_{23}H_{24}O_6$, and it contains two phenolic hydroxyl groups, one methoxyl group, and one or more amyl groups.

It dissolves in alkali hydroxides, giving unstable salts, which are decomposed by carbon dioxide and other weak acids. An alcoholic solution gives with ferric chloride a greenish-brown coloration. The addition of bromine precipitates a bromo-compound.

When oxidised with nitric acid or concentrated potassium permanganate solution it gives oxalic acid and other products, which were not identified. Fusion with potassium hydroxide gives, amongst other products, amyl alcohol, acetic, valeric, and benzoic acids.

Two crystalline derivatives have been obtained: a dimethyl derivative by the conversion of the two hydroxyl into methoxyl groups, and another derivative by the action of hydriodic acid. This reagent attacks the methoxyl group, and also has some further action, since the product contains only one hydroxyl group. It gives a methyl derivative and a monoacetyl derivative.

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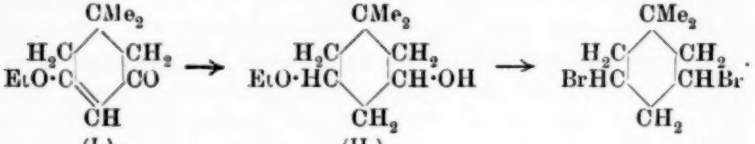
[*Received March 3rd*, 1915].

LXII.—*Dihydric Alcohols obtained by the Reduction of Substituted Dihydroresorcins.*

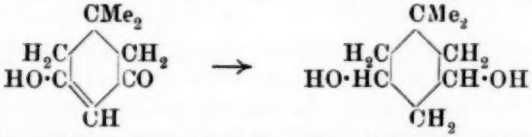
By Arthur William Crossley and Nora Renouf.

It has been shown that 1:3-dibromo-derivatives of the saturated *cyclo*hexane hydrocarbons may be used for the preparation of substituted *cyclo*hexadienes (T., 1908, **93**, 629). In the case referred to, the dibromo-compound was prepared from dimethyldihydroresorcin ethyl ether (I) by reduction, when it gave ethoxydimethyl-*cyclo*hexanol (II), which was then treated with fuming hydrobromic acid:



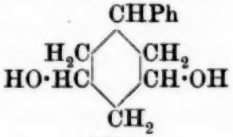
(I.) (II.)

It would appear that a more expeditious method of preparing these substances would be from the dihydric alcohols, which, on theoretical grounds, should be easily obtained by the direct reduction of the dihydroresorcins, but though many attempts have



at various times been made to bring about these reactions, in some cases resulting in the isolation of small quantities of the desired substances, it is only comparatively recently that conditions have been worked out for the preparation of the dihydric alcohols in quantity.

Knoevenagel (*Annalen*, 1895, **289**, 167) obtained small amounts of phenyl*cyclo*hexane-3:5-diol (III) by the reduction of phenyl-



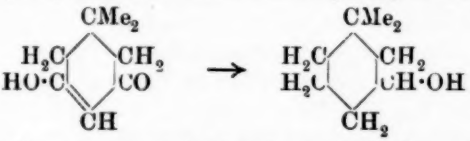
(III.)

dihydroresorcin with sodium and alcohol, and the only other paper dealing with this subject is one by Zelinski and Uspenski (*Ber.*, 1913, **46**, 1466), who also employed the same reducing agent. Numerous experiments have confirmed the fact that sodium and alcohol give the best results, and the yields are highest when the

reaction is carried out energetically by heating in an oil-bath to 110°, as stated by Zelinski and Uspenski. The amounts of the dihydric alcohols produced vary considerably with different dihydroresorcins, as is seen from the following table:

	Yield per cent.
Methyldihydroresorcin	43
Dimethyldihydroresorcin	66—68
Trimethyldihydroresorcin.....	20
*iso*Propyldihydroresorcin	40
Phenyldihydroresorcin	47—50

This is partly due to the nature of the dihydroresorcins themselves, but also to the fact that the reactions are somewhat complicated, and it is interesting to note that in all cases small quantities of the corresponding monohydric alcohols are formed; for example, 1:1-dimethyl*cyclo*hexan-3-ol from dimethyldihydroresorcin. Further, owing to the unsymmetric structure of all the molecules except that of dimethyldihydroresorcin, isomeric forms of the diols are produced, the separation of which is always tedious and sometimes has been found impracticable; for example, in the reduction of trimethyldihydroresorcin, 70 per cent. of the amount employed was isolated as a solid mixture of diols, but only 20 per cent. of this solid could be obtained as pure diol, owing to the fact that the solubilities of the two forms are so similar as to make their further separation impossible.



The dihydric alcohols are crystalline compounds, neutral to litmus, readily forming dibenzoyl derivatives, and not absorbing bromine in chloroform solution. In many properties they strongly resemble glycols, as they possess a sweet taste, are easily soluble in water, and not readily soluble in ether.

In the preparation of methyldihydroresorcin it has been noticed that when crystallised from water it separates with one molecule of water of crystallisation, and melts at 75—85°, not becoming clear until 94°, despite the fact that Knoevenagel (*Annalen*, 1895, **289**, 170) claims that it melts at 125—126°, after repeated crystallisation from hot water. The melting point is, however, easily raised to 128° by drying the crude substance in a vacuum and crystallising once from ethyl acetate.

Knoevenagel (*ibid.*, p. 167) states that he was only able to obtain a small yield of phenyl*cyclo*hexanediol by the reduction of phenyldihydroresorcin, but, if the conditions described in the experimental portion of this communication are adhered to, the yield can be

brought up to 50 per cent. of the dihydroresorcin used, and there are also obtained small quantities of phenyl*cyclo*hexanol and of a second variety of phenyl*cyclo*hexanediol, probably the *cis*-form. Each form of phenyl*cyclo*hexanediol gives one definite dibenzoyl derivative, which on hydrolysis regenerates only the particular form of the diol from which it was made.

Experimental.

Preparation of 1 : 1-*Dimethyl*cyclo*hexane*-3 : 5-*diol.*—Dimethyldihydroresorcin in quantities of 10 grams was reduced with sodium in ethyl-alcoholic solution exactly as described by Zelinski and Uspenski (*Ber.*, 1913, **46**, 1466). Instead of crystallising the crude product from a mixture of benzene and acetone, it was first distilled in a current of steam, when a small quantity of liquid, insoluble in water, passed over, which was extracted with ether, etc., and the residue (2·1 grams from three reductions) distilled in a vacuum. The main portion boiled at 102—103°/43 mm. (compare T., 1905, **87**, 1494), and was converted into the *o*-nitrobenzoyl derivative, which melted at 61—62°, nor was this melting point lowered on admixture with the *o-nitrobenzoyl* derivative of 1 : 1-*dimethyl*-cyclo*hexan*-3-*ol.* This substance has not previously been described. It may be obtained from the alcohol and *o*-nitrobenzoyl chloride in pyridine solution:

0·2915 gave 12·8 c.c. N_2 (moist) at 18° and 759 mm. N = 5·06.

$C_{15}H_{19}O_4N$ requires N = 5·05 per cent.

It is readily soluble in the cold in benzene, ethyl acetate, chloroform, or acetone, and crystallises from alcohol in radiating clusters of transparent, flattened needles, melting at 62°.

The residue from the above-mentioned steam distillation was salted out with potassium carbonate, the upper layer dissolved in alcohol, the alcoholic solution dried over potassium carbonate, and evaporated. The residue, after one crystallisation from acetone, gave dimethyl*cyclo*hexanediol in large, nacreous, scaly plates, melting at 147°, which is slightly higher than the melting point recorded by Zelinski and Uspenski. The yield is 66—68 per cent. of the theoretical, and this has not been improved upon in any of the numerous experiments carried out, despite the fact that Zelinski gives the yield as 90 per cent. A better result could not be anticipated, when it is remembered that 7—10 per cent. of the original material is recovered as dimethyl*cyclo*hexanol, and considerable quantities of resin are also formed.

The *dibenzoyl* derivative, prepared in the usual manner, is readily soluble in the cold in chloroform, benzene, or ethyl acetate, readily on warming in acetone or light petroleum (b. p. 60—80°), and

crystallises from alcohol in transparent, flattened needles, melting at 135—136°:

0·1549 gave 0·4259 CO_2 and 0·0956 H_2O. C = 74·98; H = 6·85.

$C_{22}H_{24}O_4$ requires C = 75·00; H = 6·81 per cent.

1-*Methyl*cyclo*hexane*-3:5-*diol*.

Instead of preparing methyldihydroresorcin by the method described by Schilling and Vorländer (*Annalen*, 1899, **308**, 192), the following more expeditious process was adopted.

Twenty-three grams of sodium (one atom) were dissolved in 275 c.c. of alcohol, 136 grams of ethyl acetoacetate (slight excess over 1 molecule) and 114 grams of ethyl crotonate (1 molecule) added, and the whole heated on the water-bath for seven hours. The residue was dissolved in water, the alcohol evaporated, two molecular proportions of potassium hydroxide added, and a sufficient quantity of water to make the solution contain 10 per cent. of alkali, including the atom of sodium originally used. The whole was heated to boiling in an open flask for fifteen minutes, acidified, and boiled until no more carbon dioxide was evolved. This procedure is necessary, as otherwise a poor yield of methyldihydroresorcin is obtained, due to the fact that the corresponding resorcylic acid has not been decomposed. On cooling, methyldihydroresorcin separated out in aggregates of fern-like crystals, melting at 75—85°, and not becoming clear until 94°. In this form it contains $1H_2O$, as was shown by keeping it in a vacuum, when loss in weight took place, and the resulting solid melted sharply at 126—127°:

3·0536 lost 0·3788 H_2O. H_2O = 12·40.

$C_7H_{10}O_2,H_2O$ requires H_2O = 12·5 per cent.

The dried substance, after one crystallisation from ethyl acetate, melted at 128°, and was produced in 67 per cent. of the theoretical amount.

Methyl*cyclo*hexanediol was prepared by the reduction of methyldihydroresorcin exactly as described under dimethyldihydroresorcin (see page 604). From the steam distillate methyl*cyclo*hexanol was isolated, and identified as the *o*-nitrobenzoyl derivative, melting at 54°.

For the purpose of comparison the *o-nitrobenzoyl* derivative of 1-*methyl*cyclo*hexan*-3-*ol* was prepared. It is readily soluble in the cold in acetone, ethyl acetate, benzene, or chloroform, and crystallises from light petroleum (b. p. 40—60°) in stout, colourless, transparent rhombs, melting at 54°:

0·2870 gave 13·4 c.c. N_2 (moist) at 18° and 759 mm. N = 5·38.

$C_{14}H_{17}O_4N$ requires N = 5·32 per cent.

On continuing the preparation and evaporating the dried alco-

holic solution, the residue did not show any sign of solidification after long standing, until sown with a crystal of pure methyl*cyclo*hexanediol, obtained by converting the crude material into the benzoyl derivative and hydrolysing the purified product. This process is not, however, of any use for the preparation in quantity of methyl*cyclo*hexanediol, as the solid material produced contains so much resinous matter that it will not crystallise readily from any solvent.

These facts are mentioned in order to show that the usual methods of purification were attempted before adopting the following tedious, although satisfactory, process, in which the resinous material, being insoluble in ether, remains dissolved in the aqueous solution.

The residue from the steam distillation was extracted ten times with quantities of 80—100 c.c. of ether, the ethereal solution dried with potassium carbonate and evaporated to about 50 c.c., when on sowing with a crystal of pure methyl*cyclo*hexanediol, small, colourless, transparent rhombs (1 gram) separated, melting at 74—75° (mother liquor = A). The process of extraction with ether was continued until no appreciable amount of solid was left on evaporation (five processes each consisting of ten extractions). The total pure material obtained was 4·3 grams (43 per cent. of the theoretical) from 10 grams of crude product:

0·1163 gave 0·2751 CO_2 and 0·1100 H_2O. C = 64·51; H = 10·51.
$C_7H_{14}O_2$ requires C = 64·61; H = 10·77 per cent.

1-*Methyl*cyclo*hexane*-3:5-*diol* is readily soluble in the cold in water or alcohol, readily on warming in chloroform, ethyl acetate, or acetone, and crystallises from ethyl acetate in radiating clusters of glistening needles, melting at 75°.

The *dibenzoyl* derivative is readily soluble in the cold in chloroform, benzene, ethyl acetate, or acetone, readily on warming in light petroleum (b. p. 60—80°) or alcohol, and crystallises from aqueous alcohol in small, transparent, six-sided plates, melting at 81°:

0·1893 gave 0·5183 CO_2 and 0·1116 H_2O. C = 74·67; H = 6·55.
$C_{21}H_{22}O_4$ requires C = 74·55; H = 6·50 per cent.

The mother liquors A (see above) on further evaporation gave a solid (2 grams), which when fractionally extracted with ether yielded further small quantities of the diol, and from the most insoluble portion, a substance crystallising from ethyl acetate in nacreous, flattened needles, melting at 143·5°; these probably consisted of an isomeric form of the diol, as isolated in the case of phenyl*cyclo*hexandiol (see page 610), but its amount was too small for complete characterisation.

1 : 1 : 2-*Trimethyl*cyclo*hexane*-3 : 5-*diol*.

Trimethyl*cyclo*hexanediol was obtained by the reduction of trimethyldihydroresorcin (T., 1911, **99**, 1105), employing the conditions already described (see page 604).

Trimethyl*cyclo*hexanol is produced, and by fractionating the *o*-nitrobenzoyl derivative prepared from it, there was obtained a substance melting at 114°, which proved to be identical with the *o*-nitrobenzoyl derivative of 1 : 1 : 2-trimethyl*cyclo*hexan-3-ol (*ibid.*, p. 1109).

As in the case of methyl*cyclo*hexanediol, extraction with ether was found to be the best method for isolating trimethyl*cyclo*hexanediol, which is, however, more readily soluble, and only requires two processes, each of ten extractions. The yield of pure material is 20 per cent. of the theoretical, for although the total solid from the ethereal extract is about 70 per cent. of the calculated amount, it contains another substance (probably an isomeride) so similar in solubilities that further separation has not, up to the present, been found possible:

0·1165 gave 0·2929 CO_2 and 0·1186 H_2O. C = 68·56; H = 11·31.
$C_9H_{18}O_2$ requires C = 68·35; H = 11·39 per cent.

1 : 1 : 2-*Trimethyl*cyclo*hexane*-3 : 5-*diol* is readily soluble in the cold in alcohol or acetone, readily on warming in benzene, chloroform, ethyl acetate, or water, and crystallises from either of the latter solvents in nacreous, flattened needles, melting at 150°. The *dibenzoyl* derivative crystallises from alcohol in small clusters of transparent needles, melting at 97°:

0·1340 gave 0·3720 CO_2 and 0·0832 H_2O. C = 75·71; H = 6·90.
$C_{23}H_{26}O_4$ requires C = 75·41; H = 7·10 per cent.

1-iso*Propyl*cyclo*hexane*-3 : 5-*diol*.

*iso*Propyl*cyclo*hexanediol was obtained by reducing *iso*propyldihydroresorcin (this vol., p. 173), using the same conditions as previously described (see p. 604). As the dihydroresorcin crystallises with $1H_2O$, it is necessary to remove this water by keeping for some time in a vacuum desiccator.

The viscid, reddish-brown liquid product, possessing a pungent odour, was distilled in a current of steam (residue = B), the distillate extracted with ether, and the residue, amounting to 25 per cent. of the dihydroresorcin used, fractionally distilled in a vacuum. It boiled from 140° to 170°/56 mm., and from the lowest fraction, on treatment with *o*-nitrobenzoyl chloride, there was isolated the *o*-nitrobenzoyl derivative of 1-*iso*propyl*cyclo*hexan-3-ol, melting at

48—49° (this vol., p. 174). The higher fractions of the crude product were investigated, but no definite substance was isolated.

The residue B (see above) of the steam distillation was extracted with ether (in which solvent the diol is appreciably less soluble than the homologues previously mentioned in this communication) as described under methyl*cyclo*hexanediol (see p. 606), when 40 per cent. of the theoretical amount of *iso*propyl*cyclo*hexanediol was isolated; but as in the other cases already described, a second substance, probably an isomeride, is also produced, although it could not be obtained in a pure condition:

0·1178 gave 0·2958 CO_2 and 0·1202 H_2O. C = 68·48; H = 11·34.
$C_9H_{18}O_2$ requires C = 68·35; H = 11·39 per cent.

1-iso*Propyl*cyclo*hexane*-3:5-*diol* is readily soluble in the cold in ethyl alcohol, readily on warming in acetone, ethyl acetate, benzene, chloroform, or water, and crystallises from any of these solvents, preferably ethyl acetate, in radiating clusters of small, flat, transparent needles, melting at 124°.

The *dibenzoyl* derivative is readily soluble in the cold in the usual organic solvents except light petroleum (b. p. 40—60°) and ethyl alcohol, from which it separates in radiating clusters of transparent needles, melting at 84°:

0·1018 gave 0·2823 CO_2 and 0·0639 H_2O. C = 75·62; H = 6·97.
$C_{23}H_{26}O_4$ requires C = 75·41; H = 7·10 per cent.

1-*Phenyl*cyclo*hexane*-3:5-*diol*.

Phenyl*cyclo*hexanediol was prepared by the reduction of phenyldihydroresorcin (Vorländer, *Ber.*, 1894, **27**, 2054; and Michael, *ibid.*, p. 2126), which is most expeditiously obtained in 85 per cent. of the theoretical amount from ethyl malonate and styryl methyl ketone (benzylideneacetone), using the conditions described under the preparation of methyldihydroresorcin (see p. 605).

The steam distillate was saturated with potassium carbonate, when a solid separated (0·6 gram from 20 grams of the dihydroresorcin), which crystallised from light petroleum (b. p. 80—100°) in radiating clusters of colourless, transparent needles, melting at 81°, nor was this melting point lowered on admixture with 1-*phenyl*-cyclo*hexan*-3-*ol* * prepared for the purposes of comparison.

The residue from the steam distillation, which contained an insoluble oil, was extracted *once* with ether, when immediately a quantity of white crystals separated from the aqueous liquid, melting sharply at 159°. This was filtered off, and the process of extraction with ether continued as already described (see p. 606). The combined ethereal extracts were evaporated to a small bulk,

* This substance will be described in detail in a future communication.

when further quantities of the substance melting at 159° were obtained, amounting in all to 47—50 per cent. of the phenyldihydroresorcin used. The substance had all the properties of 1-phenyl-*cyclo*hexane-3:5-diol described by Knoevenagel (*Annalen*, 1895, **289**, 167), except that after crystallisation from ethyl acetate, from which solvent it separated in nacreous leaflets, it melted at 160° instead of 157°.

Benzoyl Derivative.—Knoevenagel (*ibid.*, p. 168) states that he was unable to obtain definite diacetyl or dibenzoyl derivatives, and when the above-prepared substance was benzoylated in the usual manner, slightly more than the theoretical amount of a dibenzoyl derivative was always obtained, which, although crystallising from alcohol, aqueous alcohol, ethyl acetate, a mixture of chloroform and light petroleum, or xylene in glistening, transparent needles, did not possess a sharp melting point. It diminished in bulk at about 95—108°, melted at 108—111°, and did not become clear until 125—127°. Finally, the substance was prepared by allowing the diol and benzoyl chloride to react in pyridine solution. The whole was poured into absolute alcohol, and crystallised from the same solvent, when it again formed glistening, transparent needles, softening at 110—114°, melting at 114—115°, but not becoming clear until 127°:

0·1494 gave 0·4184 CO_2 and 0·0898 H_2O. C = 76·37; H = 6·67.

$C_{26}H_{24}O_4$ requires C = 78·00; H = 6·00 per cent.

$(C_{26}H_{24}O_4)_2,C_2H_5\cdot OH$ requires C = 76·59; H = 6·38 per cent.

The fact that the substance is always produced in rather more than the theoretical amount would indicate that it crystallises with solvent of crystallisation, which supposition is borne out by the above analysis. It was, nevertheless, not found possible to drive off the solvent either by keeping in a vacuum or by heating to 100° for some time. Similar instances of compounds crystallising with solvent of crystallisation, which could not be eliminated, have been recorded by Morgan and Micklethwait (T., 1908, **93**, 615) and by Cain and Micklethwait, (T., 1914, **105**, 1438).

When this benzoyl derivative was hydrolysed with alcoholic potassium hydroxide it gave the original phenyl*cyclo*hexanediol (m. p. 160°) in theoretical amount.

The ethereal mother liquors from which the diol (m. p. 160°) had crystallised out were completely evaporated, leaving a reddish-yellow resin, which was boiled with water and filtered while hot, from a small amount of insoluble material, allowed to cool, and extracted ten times with ether. On evaporating to a small bulk a white solid separated, which was crystallised from water (0·7 gram from 20 grams of phenyldihydroresorcin) and analysed:

0·1614 gave 0·4425 CO_2 and 0·1172 H_2O. C = 74·77; H = 8·07.
$C_{12}H_{16}O_2$ requires C = 75·00; H = 8·33 per cent.

1-*Phenyl*cyclo*hexane*-3:5-*diol*, probably the *cis*-modification, is sparingly soluble in benzene or chloroform on warming, more soluble in water, and readily soluble in ethyl acetate, acetone, or alcohol; in fact, in these respects it is identical with the variety melting at 160°. It crystallises from ethyl acetate or water in radiating clusters of nacreous, scaly needles, melting at 134°.

The *dibenzoyl* derivative, prepared in the usual manner, crystallises from alcohol in radiating clusters of small, silken needles, melting at 117°:

0·1053 gave 0·3025 CO_2 and 0·0547 H_2O. C = 78·34; H = 5·77.
$C_{26}H_{24}O_4$ requires C = 78·00; H = 6·00 per cent.

This benzoyl derivative is produced in theoretical amount, and when hydrolysed regenerates quantitatively the phenyl*cyclo*hexane-diol, melting at 134°.

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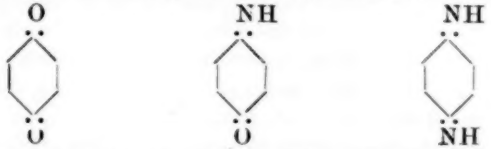
[*Received April 12th*, 1915.]

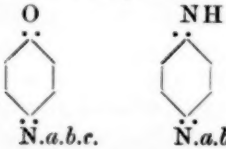
LXIII.—*Alkylated Para-phenylenediamines and Derivatives. Quinoneimide–Ammonium Compounds.*

By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

THE well-known relationship between quinone, quinone-imide, and



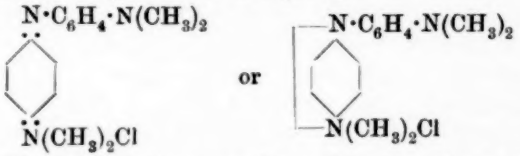
quinone-di-imide points to the possible existence of a class of compounds similarly related to the quinone-ammonium compounds which have formed the subject of numerous communications to the Society during the last three years:



(or alternative cross-linkage).

Quinoneimide-ammonium compounds of the above type have long been known in tinctorial chemistry. The colouring matters classed

as indamines may, in fact, be regarded as derivatives of the hypothetical parent substance indicated by the above formula, Bindschedler's green (*Ber.*, 1883, **16**, 865) being one of the first discovered coloured compounds of the group:



Although these indamines may be referred to the quinoneimide-ammonium type, the analogy between these coloured compounds and the true quinone-ammonium derivatives is strictly valid only when *a*, *b*, *c*, in the above formula are all represented by organic radicles. The present research was undertaken with the object of preparing compounds of the true quinoneimide-ammonium type with special reference to those derivatives in which *a*, *b*, and *c* are represented by different radicles. Such compounds might be expected to be resolvable into optically active isomerides. We have succeeded in obtaining one compound belonging to the simpler type, in which *a*, *b*, and *c* all stand for CH_3, but the preparation of derivatives containing an asymmetric quinquevalent nitrogen atom has presented great difficulties, and the results are as yet inconclusive.

Quinoneimide-ammonium compounds of the required type may be regarded as inner anhydrides or condensation products of amino-ammonium hydroxides or salts:

$$C_6H_4\!<\!\begin{matrix}NH_2\\N.a.b.c.OH\end{matrix} - H_2O \longrightarrow C_6H_4\!\ll\!\begin{matrix}NH\\N.a.b.c.\end{matrix}$$

$$C_6H_4\!<\!\begin{matrix}NH_2\\N.a.b.c.X\end{matrix} - HX \longrightarrow C_6H_4\!\ll\!\begin{matrix}NH\\N.a.b.c.\end{matrix}$$

The preparation of the parent amino-ammonium compounds could not, of course, be attempted by the direct alkylation of the unsymmetrical dialkylated diamines, $C_6H_4\!<\!\begin{matrix}NH_2\\N.a.b.\end{matrix}$, since the unsubstituted amino-group would certainly be attacked by the alkylating agents. Two methods were therefore tried:

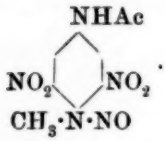
(1) The alkylation of *p*-nitroaniline so as to prepare $C_6H_4\!<\!\begin{matrix}NO_2\\N.a.b.\end{matrix}$, from which it was hoped to obtain $C_6H_4\!<\!\begin{matrix}NO_2\\N.a.b.c.X\end{matrix}$ by the usual methods; the latter on reduction and removal of HX would give the required compounds.

(2) The acylation of the unsubstituted amino-group in the dialkyl-diamine so as to obtain $C_6H_4\!<\!\begin{matrix}NH\cdot Ac\\N.a.b.\end{matrix}$ which, by the addi-

tion of alkyl iodides, might be expected to give compounds of the type $C_6H_4<^{NH\cdot Ac}_{N.a.b.c.X}$, from which the required quinoneimide-ammonium compounds might be prepared.

The first of these methods has hitherto been unsuccessful, a fact which is in itself of some interest, as the presence either of the para-nitro-group or the benzyl group appears to prevent the dialkylamino-group from alkylation into a quaternary (trialkyl) ammonium group. The second method, on the other hand, has proved to be quite successful, the para-acetylamino-group appearing to facilitate the formation of ammonium compounds by the nitrogen atom of the dialkylamino-group. It is obvious that by this method the synthesis of numbers of compounds containing an asymmetric quinquevalent nitrogen atom becomes possible, the addition of *c*X to the N.*a.b*-group giving rise to compounds containing the group N.*a.b.c*.X, in which *a*, *b*, and *c* may be dissimilar radicles.

The investigation of the dialkylphenylenediamines required for the present research has resulted in the discovery of certain new and interesting properties of these compounds which are described in the experimental part of this paper. Attention is directed more especially to the nitration products of the acetyl derivatives of the dialkylated diamines. Compounds of the type $C_6H_4<^{NH\cdot Ac}_{N.a.b.}$ all give on nitration the same product, the dinitronitrosoamine of the constitution:



It thus appears that whatever radicles may be attached to the 4*N*-atom, methyl alone is retained, the heavier radicles being expelled and replaced by the nitroso-group. This fact has been established for the dimethyl, methylethyl, and benzylmethyl compounds, all of which give the above nitrosoamine.

Experimental.

The discovery that all the dialkylated acetyl-*p*-phenylenediamines gave the same product on nitration and the determination of the constitution of this product resulted mainly from the detailed investigated of the methylethyl compound:

*Methylethylacetyl-*p*-phenylenediamine* (p-*Methylethylamino-acetanilide*), $NHAc\langle\bigcirc\rangle N(CH_3)\cdot C_2H_5$.

Methylethylaniline was converted into its nitroso-derivative by adding the calculated quantity of sodium nitrite dissolved in water to a solution of the hydrochloride of the base cooled in ice. The nitroso-hydrochloride after purification was reduced by tin and hydrochloric acid, the tin removed as sulphide, and the solution containing the methylethyl-*p*-phenylenediamine hydrochloride evaporated to dryness after removing free hydrogen sulphide by passing a stream of carbon dioxide through the solution.* The hydrochloride forms a syrup, which solidifies partly to a crystalline pulp on keeping. Acetylation was effected by heating the hydrochloride with anhydrous sodium acetate and acetic anhydride on a water-bath. After decomposing the excess of acetic anhydride by hot water the base was precipitated by neutralising the solution of the acetate with ammonia; it separates as a resin, which solidifies to a crystalline mass on cooling. The product was purified by crystallisation from dilute alcohol with the addition of animal charcoal, and consisted of colourless, silky needles, melting at 92°:

0·0997 gave 12·7 c.c. N_2 (moist) at 18° and 749·3 mm. N = 14·50.
$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

This acetylamino-compound combines readily with alkyl iodides to form quaternary ammonium iodides. Combination takes place at the ordinary temperature after some hours, and more rapidly on heating. *iso*Propyl iodide is exceptional among the alkyl iodides experimented with, no combination taking place when this compound is used. The ammonium iodides are beautifully crystalline substances, soluble in water, and having all the properties pertaining to compounds of this group. The analytical results clearly indicated that dissociation of the iodides takes place on crystallisation from alcohol or water, and no more stable salts have as yet been prepared. The bases formed by decomposing the iodides with moist silver oxide in the usual way are syrupy compounds which absorb carbon dioxide from the air, and form uncrystallisable carbonates on evaporation of their solutions.

In view of the special interest attaching to the ammonium derivatives containing an asymmetric nitrogen atom the two compounds containing propyl and allyl respectively have been prepared and studied in some detail. These compounds are:

* This precaution is necessary in order to prevent loss due to the formation of the homologue of methylene-blue by oxidation during the evaporation.

$NHAc{\cdot}C_6H_4{\cdot}NI(CH_3)(C_2H_5){\cdot}C_3H_7$.
Methylethylpropyl-4-acetylaminophenyl-ammonium iodide.

$NHAc{\cdot}C_6H_4{\cdot}NI(CH_3)(C_2H_5){\cdot}C_3H_5$
Methylethylallyl-4-acetylaminophenyl-ammonium iodide.

These substances are no doubt resolvable into optically active isomerides, but the research has not yet been developed in this direction as all the salts with optically active acids so far studied appear to be non-crystalline syrups or resins. The acetyl group is readily removed by acid hydrolysing agents, with the formation of salts of the aminophenylammonium bases. Attempts to prepare quinoneimide-ammonium compounds and their nitro-derivatives from these last bases have so far been unsuccessful, but this branch of the research will be continued. These aminophenylammonium compounds may also serve as starting points for the synthesis of quinoneammonium derivatives containing an asymmetric nitrogen atom, preliminary experiments having shown that the amino-group is readily diazotisable. The removal of the acetyl group can be effected by boiling the base with dilute sulphuric acid or by repeated evaporation with concentrated hydrobromic acid. The compound containing methyl, ethyl, and propyl, when submitted to this last treatment, left a *dibromide*,

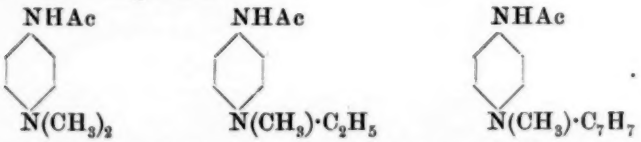
$$HBr,NH_2{\cdot}C_6H_4{\cdot}NBr(CH_3)(C_2H_5){\cdot}C_3H_7,$$

crystallising in colourless tablets:

0·2463, dried at 100°, gave 0·2619 AgBr. Br = 45·26.
$C_{12}H_{21}N_2Br,HBr$ requires Br = 45·16 per cent.

*Nitration of the Dialkylacetyl-*p*-phenylenediamines.*

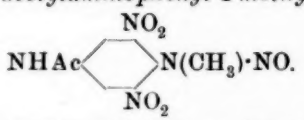
The three compounds:



as already stated, all give the same product on nitration. In order to prepare this compound the dialkylacetyl derivative is dissolved in a small quantity of glacial acetic acid, the solution cooled in ice, and fuming nitric acid diluted with twice its volume of glacial acetic acid added in small portions. The nitric acid acts very energetically at first, but more sluggishly as the quantity is increased. In order to complete the nitration an excess of nitric acid is required, and the solution must be taken from the ice-bath and allowed to remain at the atmospheric temperature for about an hour. The nitro-derivative partly separates in a crystalline

form from the acetic acid solution, and is completely precipitated on stirring the solution into water. The course of the nitration can be followed by withdrawing a drop of the solution from time to time, and diluting with water on a watch-glass; as long as the nitration is incomplete the product which separates on applying this test is resinous, but becomes white and crystalline when the nitration is complete. Attempts to isolate definite intermediate products resulting from the action of nitric acid have been unsuccessful. By the action of nitrous acid on the dimethylacetyl derivative a definite crystalline compound (red, stumpy prisms, m. p. 132—133°; N = 19·31) has been obtained, but the study of this substance, which does not appear to be a nitrosoamine, has not been completed.

3 : 5-*Dinitro*-1-*acetylaminophenyl*-4-*methylnitrosoamine*,



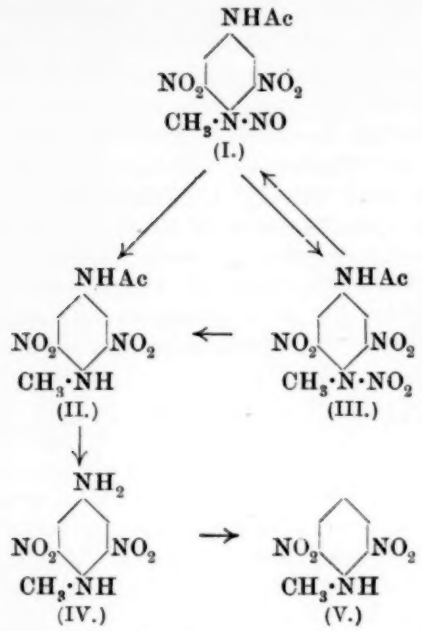
The product of nitration obtained as described has been proved to have the above constitution by methods described later in this paper. It crystallises from alcohol, in which it is readily soluble, in stumpy prisms, in tablets, or in scales, according to the rate of deposition. The compound is colourless, and melts at 152—153°. It gives the Liebermann reaction for the nitroso-group with sulphuric acid and phenol. The identity of the product from all three sources was proved by analysis, melting point, and mixed melting points:

0·1042 gave 0·1450 CO_2 and 0·0310 H_2O. C = 37·95; H = 3·30.
0·1004 „ 0·1400 CO_2 „ 0·0305 H_2O. C = 38·03; H = 3·37.
0·0936 „ 20·3 c.c. N_2 (moist) at 15·5° and 746·9 mm. N = 24·89.
0·1322 gave 28·0 c.c. N_2 (moist) at 16·5° and 761·3 mm. N = 24·67.
$C_9H_9O_6N_5$ requires C = 38·15; H = 3·20; N = 24·74 per cent.

The evidence on which the above constitutional formula is based is summarised in the scheme on p. 616.

The dinitronitrosoamine on boiling for about half-an-hour with absolute phenol loses its nitroso-group, and is converted into the dinitromethylacetyl-*p*-phenylenediamine (II). This last compound crystallises from alcohol in small, scarlet needles, melting at 196—197°:

0·1041 gave 0·1610 CO_2 and 0·0385 H_2O. C = 42·18; H = 4·11.
0·0885 „ 17 c.c. N_2 (moist) at 21·5° and 769·9 mm. N = 22·11.
$C_9H_{10}O_5N_4$ requires C = 42·5; H = 3·97; N = 22·05 per cent.



The bright red colour of this compound suggests, in accordance with our former conclusions concerning the relationship between colour and constitution (T., 1914, **105**, 414), that its constitution is that of an inner salt:

The dinitronitrosoamine dissolves in fuming nitric acid (cooled to 0°) with the formation of the corresponding nitroamine (III). The oxidation of the nitroso-group was effected by dissolving 3 grams of the nitrosoamine in 25 c.c. of cooled fuming nitric acid, removing the solution from the ice-bath, and allowing to remain at the atmospheric temperature for an hour. The product was isolated by precipitation with water, collecting and washing and crystallising from alcohol, from which it separates in tufts of white needles forming fern-like groups, melting at 183—184°:

0·10 gave 0·1312 CO_2 and 0·0274 H_2O. C = 35·78; H = 3·04.
0·1005 ,, 20·5 c.c. N_2 (moist) at 16° and 751·4 mm. N = 23·51.
$C_9H_9O_7N_5$ requires C = 36·11; H = 3·03; N = 23·42 per cent.

The compound has all the properties of a nitroamine; boiling phenol converts it into the dinitromethylacetyl-*p*-phenylenediamine melting at 196—197°. A solution of the substance in glacial acetic acid containing a little α-naphthylamine develops a reddish-violet colour on heating with a fragment of zinc (Franchimont-Bamberger reaction). The substance dissolves in concentrated sulphuric acid, and the solution, after being kept at the atmospheric temperature for an hour, gives the original nitrosoamine (m. p. 152—153°) on dilution with water (Reverdin's reaction).

3:5-Dinitromethyl-*p*-phenylenediamine (IV) was obtained from its acetyl derivative by heating the latter with concentrated sulphuric acid diluted with a few drops of water until a drop of the solution remained clear on dilution with water. At this stage hydrolysis is complete, and on pouring the solution into water the sulphate of the base remains dissolved. The free base is precipitated as a deep purple, flocculent substance on neutralisation of the acid solution with ammonia. After being collected, washed with water, and crystallised from dilute alcohol, the compound consists of dark purple needles, having a green lustre by reflected light, and melting at 186—187°:

0·1128 gave 0·1637 CO_2 and 0·040 H_2O. C = 39·58; H = 3·94.

0·1074 ,, 24·7 c.c. N_2 (moist) at 20·5° and 761·2 mm. N = 26·28.

$C_7H_8O_4N_4$ requires C = 39·6; H = 3·8; N = 26·42 per cent.

The compound is distinctly basic, and displays remarkable colour changes under various conditions. The intense colour of the free base is in harmony with the view that, like its acetyl derivative (VI), it has the "inner salt" structure (VII). It dissolves in dilute acids with a yellow colour, the solution at this stage probably containing the di-acid salt. On dilution with water the solution becomes pink, probably owing to the formation of the mono-acid salt by dissociation. The addition of alkali causes the immediate development of the intense purple colour of the free base. The colour change is strikingly sharp, and the compound would, no doubt, be useful as an indicator.

The constitution of this dinitromethyl-*p*-phenylenediamine was determined by replacing the amino-group by hydrogen by the diazo-method, as described in the following section, the product being 2:6-dinitromethylaniline (V).

*Dimethylacetyl-*p*-phenylenediamine* (*Dimethylamino-*p*-acetanilide*).

This compound was prepared from nitrosodimethylaniline by reduction and acetylation of the hydrochloride of the base in the same way as described for the methylethyl derivative. The pure

substance crystallised from water consisted of slender, white needles melting at 132—133° (130°, Beilstein, IV, 588). Combination with methyl iodide takes place when the compound is covered with methyl iodide and allowed to remain at the ordinary temperature in a closed vessel for three to four days. The methiodide,

$$NHAc{\cdot}C_6H_4{\cdot}NI(CH_3)_3$$

(4-acetylaminophenyltrimethylammonium iodide), crystallises from water in dense, colourless prisms, which have the usual tendency to dissociate on crystallisation. The ammonium hydroxide base prepared by means of silver oxide in the usual way is an alkaline syrup which carbonates on exposure to the air. A *picrate*,

$$NHAc{\cdot}C_6H_4{\cdot}N(CH_3)_3{\cdot}O{\cdot}C_6H_2(NO_2)_3,$$

was prepared by adding an alcoholic solution of picric acid to an aqueous solution of the base. The salt separates in yellow scales melting at about 206—208° with a considerable range of preliminary softening:

0·1373 gave 20·5 c.c. N_2 (moist) at 16·5° and 729·6 mm. N = 16·65.
$C_{17}H_{19}O_8N_5$ requires N = 16·63 per cent.

A definite *ferrocyanide* was obtained by dissolving the methiodide in water, adding a solution of potassium ferrocyanide in excess, and acidifying with hydrochloric acid. A crystalline pulp of slender, white needles formed after some hours. This salt, after being collected, washed with water, and dried at 100°, had the composition $[NHAc{\cdot}C_6H_4{\cdot}N(CH_3)_3]_2,H_2Fe(CN)_6,2H_2O$:

0·1053 gave 0·2037 CO_2, 0·0569 H_2O, and 0·0134 Fe_2O_3.
C = 52·76; H = 6·0; Fe = 8·91.

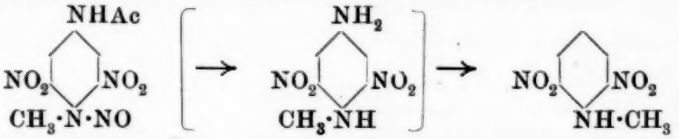
0·3046 gave, on ignition in air, 0·0384 Fe_2O_3. Fe = 8·83.
0·0842 „ 16 c.c. N_2 (moist) at 17° and 761·5 mm. N = 22·09.
$(C_{11}H_{17}ON_2)_2,H_2Fe(CN)_6,2H_2O$ requires C = 52·8; H = 6·33;
N = 22·02; Fe = 8·77 per cent.

The salt does not lose water at 100°, and at higher temperatures decomposition takes place, resulting in a loss of weight greater than that required theoretically for the expulsion of two molecules.

Action of Alcoholic Hydrochloric Acid on the Dinitronitrosoamine.

A supply of the nitrosoamine having been prepared from dimethylacetyl-*p*-phenylenediamine by nitration in the way previously described, an attempt was made to remove the nitroso-group by boiling the compound with alcoholic hydrochloric acid. The study of the ensuing reaction led to the discovery that every possible change takes place, the nitroso- and acetyl groups being eliminated, and the amino-group at the same time being replaced

by hydrogen, the final product being 2:6-dinitromethylaniline, melting at 106° (Bamberger, *Ber.*, 1897, **30**, 1257):



This result determines the constitution of the dinitronitrosoamine and nitroamine, and of the dinitromethyl-*p*-phenylenediamine. The reaction results in the removal of acetyl and the nitroso-group, the diazotisation of the dinitromethyl-*p*-phenylenediamine by the latter, and the decomposition of the diazonium salt by alcohol. The intermediate stages are passed through rapidly under the conditions imposed, namely, the heating of the solution of the nitrosoamine in absolute alcohol with the addition of a little concentrated hydrochloric acid until the decomposition commences. The reaction then continues spontaneously with brisk evolution of nitrogen and the formation of aldehyde, and is completed by boiling the solution for about an hour with reflux condensation. On diluting the cold solution with water the dinitromethylaniline separates in dull orange needles, which are purified by crystallisation from hot water, and then melt at 106—107°:

0·0866 gave 15·9 c.c. N_2 (moist) at 17° and 761·6 mm. N = 21·34.
$C_7H_7O_4N_3$ requires N = 21·33 per cent.

This dinitromethylaniline when acted on by nitrous acid (sodium nitrite) in cooled acetic acid solution forms a nitrosoamine (2:6-*dinitrophenyl*-1-*methylnitrosoamine*), which crystallises from alcohol in white needles melting at 115—116°:

0·0892 gave 19·4 c.c. N_2 (moist) at 21° and 761·5 mm. N = 24·8.
$C_7H_6O_5N_4$ requires N = 24·79 per cent.

That the above interpretation of the action of alcoholic hydrochloric acid on the dinitronitrosoamine is correct was proved by diazotising dinitromethyl-*p*-phenylenediamine in dilute sulphuric acid solution, and boiling the diazonium sulphate with alcohol. The solution, on completion of the reaction, gave on dilution with water the 2:6-dinitromethylaniline described.

Benzylmethylacetyl-p-*phenylenediamine* (p-*Benzylmethylaminoacetanilide*).

p-Nitroaniline was converted into its monobenzyl derivative by the method described in 1888 (Meldola and Salmon, T., **53**, 774), and the product methylated by heating with excess of methyl sulphate at 100° for two hours. After removing the excess of methyl sulphate by heating the solution alternately with dilute

hydrochloric acid and alkali and washing with water the resulting compound was obtained pure by crystallisation from methyl alcohol.

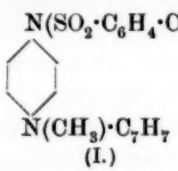
Benzylmethyl-p-*nitroaniline* crystallises in silky, yellow needles, melting at 68—69°:

0·1144 gave 0·2915 CO_2 and 0·0630 H_2O. C = 69·49; H = 6·12.

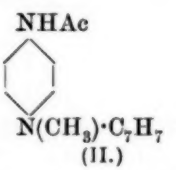
$C_{14}H_{14}O_2N_2$ requires C = 69·37; H = 5·8; N = 11·57 per cent.

All attempts to prepare ammonium derivatives from this compound led to negative results. Methyl and ethyl sulphates leave the benzylmethylamino-group unchanged, and heating with alkyl iodides results in the detachment of benzyl.

The base, *benzylmethyl*-p-*phenylenediamine*, was obtained from the foregoing compound by reduction with tin and hydrochloric acid in the usual way. The hydrochloride separates in white needles on concentrating the solution after removal of the tin as sulphide. In order to characterise the compound a toluenesulphonamide was prepared by agitating a hot aqueous solution of the hydrochloride with alkali and toluenesulphonyl chloride. A product insoluble in alkali was finally obtained, and this on analysis proved to be the di-derivative (I):



(I.)



(II.)

This compound crystallises from glacial acetic acid in colourless scales melting at 217°:

0·1626 gave 7·7 c.c. N_2 (moist) at 14° and 767 mm. N = 5·62.

0·2016 „ 0·1806 $BaSO_4$. S = 12·30.

$C_{28}H_{28}O_4N_2S_2$ requires N = 5·39; S = 12·34 per cent.

The *acetyl* derivative (II) was prepared from the hydrochloride by the action of acetic anhydride and sodium acetate in the usual way. It crystallises from dilute alcohol in slender, white, silky needles, melting at 110—111°:

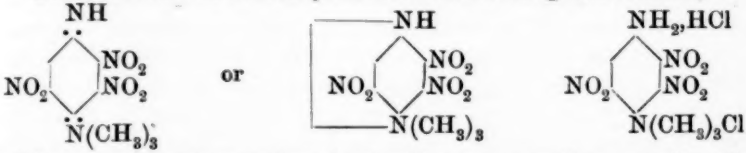
0·1564 gave 15·1 c.c. N_2 (moist) at 19·5° and 772 mm. N = 11·25.

$C_{16}H_{18}ON_2$ requires N = 11·02 per cent.

This acetyl derivative, unlike those containing methyl and ethyl, fails to give quaternary ammonium iodides with alkyl iodides, the presence of the benzyl group apparently preventing the formation of these compounds. If heated with alkyl iodides to temperatures above 100° benzyl is split off. Negative results were obtained with propyl and allyl iodides, both of which combine readily with the dialkylacetyl derivatives previously described. Benzylmethylacetyl-

p-phenylenediamine can be nitrated in acetic acid solution with the formation of the same dinitrophenylmethylnitrosoamine as that obtained from the other dialkyl derivatives. The benzyl is split off as benzaldehyde, the nitric acid acting also as an oxidising agent.

2 : 3 : 5-*Trinitro*-4-*trimethylammonium*-1-*benzoquinoneimide*,



After numerous experiments leading to negative results the above compound has been obtained as the first representative of the true quinoneimide-ammonium derivatives. The simpler unsubstituted compounds of this type have not yet been isolated, and unsatisfactory results have been obtained with derivatives containing radicles other than methyl. We hope to be able to extend the research in the required direction so as to obtain compounds containing an asymmetric quinquevalent nitrogen atom.

In order to prepare the above compound, dimethylacetyl-*p*-phenylenediamine was converted into its methiodide, and the latter into the nitrate by decomposition with silver nitrate. The trimethylammonium nitrate, $NHAc{\cdot}C_6H_4{\cdot}N(CH_3)_3{\cdot}NO_3$, crystallises from alcohol, in which it is extremely readily soluble, in flat, colourless needles decomposing over a wide range of temperature reaching finally 225°. Partial dissociation takes place during crystallisation (Found, N = 17·26. Calc., N = 16·47 per cent.). The nitrate was nitrated by dissolving in a cold mixture of fuming nitric and concentrated sulphuric acid, and testing the solution from time to time by diluting a drop with water on a watch-glass. The appearance of a yellow, crystalline deposit indicates that the nitration is complete, the process requiring for its completion about three or four hours at the ordinary atmospheric temperature. If the solution is allowed to stand too long the yield of nitro-derivative decreases. The product is isolated by pouring the nitrating solution on ice, and collecting the precipitate, washing with water, and finally with alcohol, in which the compound is practically insoluble. It crystallises in small, golden-yellow scales having no definite melting point, but decomposing at 200° to 220°:

0·1003 gave 0·1385 CO_2 and 0·0312 H_2O. C = 37·66; H = 3·45.
0·3191 „ 0·4398 CO_2 „ 0·1096 H_2O. C = 37·59; H = 3·82.
0·1502 „ 0·2066 CO_2 „ 0·0534 H_2O. C = 37·51; H = 3·95.
0·1101 „ 23·7 c.c. N_2 (moist) at 20·5° and 756·5 mm. N = 24·44.

$C_9H_{11}O_6N_5$ requires C = 37·88; H = 3·89; N = 24·57 per cent.

The compound has the properties attributable to a quinoneimide derivative, but a more detailed study will be necessary in order to confirm the constitution assigned. The only doubtful position is that given to the third nitro-group which is assumed to be in position 5 (instead of 6) by virtue of the analogy to the product of nitration of the dialkylacetyl derivatives previously shown to have the nitro-groups in positions 3 and 5. The quinoneimide-ammonium compound dissolves in cold hydrochloric acid with the formation of a salt of the type shown in the above formula. The solution of the salt is colourless, and the yellow quinoneimide crystallises out unchanged on neutralisation with alkali. This quinoneimide is unstable, and no definite derivatives have as yet been obtained. The acid solution if heated to near its boiling point decomposes with the evolution of gas, and the formation of a crystalline substance volatile in steam. These products have not yet been examined in detail, as the original compound is difficult to prepare in quantity, and the yield of decomposition products is extremely small. There can be no doubt, however, that the decomposition of the quinoneimide by heating with acids is the result of the complete disruption of the benzene ring. The ring-system appears to break down also when the nitro-groups are completely reduced by tin and hydrochloric acid.

In carrying out the foregoing research we have received valuable assistance from Mr. H. S. Foster, to whom we desire to express our thanks. We are indebted also to the firm of Read Holliday and Sons, Ltd., of Huddersfield, for supplies of many of the materials required for our work.

City and Guilds Technical College,
Finsbury. [*Received, April 21st*, 1915.]

LXIV.—*The Action of Stannous Chloride on Sulphuric Acid and on Sulphurous Acid.*

By Reginald Graham Durrant.

In 1792 Pelletier (*Ann. Chim. Phys.*, 1792, [i], **12**, 231) observed that a solution of tin in hydrochloric acid did not appear to have any action on sulphuric acid, but decomposed sulphurous acid, yielding sulphur and tin oxide. Girardin (*Ann. Chim. Phys.*, 1836, **61**, 286) extended Pelletier's work, and used the reaction as a test for sulphur dioxide in samples of hydrochloric acid. He

observed the odour of hydrogen sulphide in the reaction, and regarded the change as due to the formation of stannic chloride, leaving the metal which then formed stannic oxide and stannous sulphide on reacting with sulphurous acid; the stannous sulphide then produced hydrogen sulphide by action with hydrochloric acid.

Hering (*Ann. Pharm.*, 1839, **29**, 90) regarded the reaction between stannous chloride and a hot mixture of hydrochloric and sulphurous acids as occurring in two stages, finally giving:

$$6SnCl_2 + 2SO_2 + 8HCl = 5SnCl_4 + SnS_2 + 4H_2O.$$

Fedorov (*Jahresber.*, 1869, 912) applied the reaction of stannous chloride and sulphurous acid to the precipitation of the metals arsenic, antimony, bismuth, copper, and platinum as sulphides.

Pattison Muir (*Mon. Sci.*, 1882, [iii], **12**, 783) regarded sulphurous acid as an oxidiser of stannous chloride, and called attention to the importance of the reaction in separating arsenic from tin. As mentioned, Pelletier found no action with sulphuric acid; the only reference to this action appears to be one (*Jahresber.*, 1882, 1301) in which Vogel is stated to have shown that concentrated sulphuric acid evolves but little hydrogen chloride when acting in the cold on stannous chloride, but on heating hydrogen chloride, hydrogen sulphide, sulphur dioxide, and some stannic chloride are evolved, whilst free sulphur and stannic sulphate are formed.

Sandonini and Aureggi (*Gazzetta*, 1912, **42**, i, 227) studied the action of barium, silver, and copper sulphates on anhydrous stannous chloride in an atmosphere of nitrogen; in each case a reduction of the sulphate occurred, and the production of sulphur dioxide preceded further change. The influence of an excess of hydrochloric acid in the oxidation of stannous chloride has been noticed by Vortmann and Padberg (*Ber.*, 1889, **22**, 2642), who showed that when flowers of sulphur are heated with stannous chloride in an excess of hydrochloric acid, hydrogen sulphide is evolved, and all the tin is converted into stannic chloride, and Kahlenberg (*J. Amer. Chem. Soc.*, 1894, **16**, 314) noticed that an excess of hydrochloric acid first favours a reaction of the second order between stannous chloride and ferric chloride, but sensibly interferes with the speed towards the end of the reaction.

Noyes (*Zeitsch. physikal. Chem.*, 1895, **16**, 546) observed that an excess of hydrochloric acid tends to change the nature of this reaction to the second order, although in less acid solution it approximates to the third order.

Finally, Young (*J. Amer. Chem. Soc.*, 1901, **23**, 21, 450) oxidised stannous chloride by various agents, and proved the existence of complexes of hydrochloric acid and stannous chloride which influence the rate of change. His work will be referred to later on.

Whilst not conflicting essentially with the results of previous investigators, the present work has extended them. Sulphur dioxide is the first product of the reduction of sulphuric acid by stannous chloride, as was shown for sulphates by Sandonini and Aureggi (*loc. cit.*). The temperatures between which successive changes occur when concentrated sulphuric acid acts on stannous chloride have been ascertained. The hydrogen sulphide produced when less concentrated acid is used is shown to depend on solution of sulphur dioxide. For this and other reasons the study of the action of sulphurous acid on stannous chloride forms the chief part of the paper. The changes, which have occurred at room temperature, are shown to be modified by varying conditions of concentration and admixture. Where hydrochloric acid is present in excess, the reaction in its earlier stages, like that of stannous and ferric chlorides, approximates to one of the second order.

Experimental.

The Action of Concentrated Sulphuric Acid in Excess on Hydrated Stannous Chloride.

0·815 Gram of stannous chloride ($SnCl_2$,1·85H_2O), together with 10 c.c. of concentrated sulphuric acid, was placed in a flask fitted with a delivery tube and an exit tube connected with two U-tubes in series, containing distilled water and well-washed garnets. The first U-tube also contained a drop of potassium dichromate solution as indicator; the second was connected with Mohr's bulbs also containing water.

The flask was placed in a mercury bath which was heated gradually for one hour. During the operation hydrogen, delivered so as not to pass into the acid, was passed through the whole apparatus. For the first fifteen minutes the temperature was below 15°. Surface dehydration occurred, but there was no evolution of gas. A bubble of hydrogen chloride was noted at 19°, the evolution became more brisk at 45°, and was rapid between 58° and 70°. At 75° it ceased. The temperature was raised to 84°, when the burner was removed. The current of hydrogen was maintained for another hour as the flask cooled down. There was no tinge of green in the first U-tube, hence sulphur dioxide had not been evolved below 84°. The contents of the U-tubes and bulbs were evaluated for hydrogen chloride by $N/2·5$-sodium carbonate. There was some loss by fuming from the first U-tube, and some hydrogen chloride was retained by the sulphuric acid at 84°, but 83·4 per cent. of the calculated amount was estimated. In the second part of the experiment the U-tubes and Mohr's bulbs contained 20 c.c.

of N-potassium dichromate, the flask with its now cold contents being fitted as before. The mercury-bath was heated gradually while hydrogen passed through. A bubble was seen on the glass at 130°, but no bubbles of any gas escaped below 170°. The evolution was brisker at 175°, and still more so at 180°. The bath was kept at this temperature for some time, and then at 190° for fifteen minutes, during which period no further evolution occurred. The flame was then removed, and the apparatus allowed to cool in a current of hydrogen.

The contents of the U-tubes and bulbs were washed out, and the excess of dichromate was estimated by thiosulphate after treatment with potassium iodide. The volume of $N/10$-sodium thiosulphate required was 127·3 c.c. By calculation for the reaction:

$$SnSO_4 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O + SO_2,$$

129·8 c.c. would be required. The result indicated that 1·9 per cent. more sulphur dioxide was evolved than would be due to the reaction. The U-tubes had both been surrounded by cold water, but the hot hydrogen might have caused a slight reduction in the first tube. The diluted contents of the flask decolorised 0·23 c.c. of $N/2$-permanganate, indicating that either 1·5 per cent. of sulphur dioxide was retained or 1·5 per cent. of tin had escaped oxidation. A preliminary experiment had indicated all the results here given, and had proved that stannous chloride was entirely converted into stannic sulphate after heating at 200°. Hence the reaction:

$$SnCl_2 + H_2SO_4 = SnSO_4 + 2HCl$$

occurs, and is completed below 90°. The further action yielding stannic sulphate and sulphur dioxide occurs, and is completed between 130° and 200°.

The Action of Heat on Stannous Sulphate.

Some silky crystals of stannous sulphate, prepared by digesting stannous chloride with less concentrated sulphuric acid, were heated in a hard glass tube to dull redness:

0·1387 gave 0·0960 SnO_2. $SnO_2 = 69·93$.

The reaction $SnSO_4 = SnO_2 + SO_2$ requires $SnO_2 = 70·23$ per cent. The analysis of samples of freshly purchased stannous sulphate confirms this result, and showed that the action is the same in the presence or absence of air. The reaction was shown to occur between 360° and red-heat temperature, since, when stannous sulphate was heated in a tube surrounded by the vapour of boiling mercury for forty-five minutes, sulphur dioxide was evolved, although only to the extent of 1·3 per cent. This action starts at a lower temperature than that at which ferrous sulphate is converted into ferric oxide.

The Action of Dilute Sulphuric Acid on Stannous Chloride.

Many experiments were made on the action of sulphuric acid on solutions of stannous chloride, with and without hydrochloric acid. The earlier experiments were performed with a carefully prepared solution obtained by the action of hydrochloric acid on pure tin in the presence of platinum, the solution being preserved in an atmosphere of hydrogen. Subsequently the hydrogen was omitted, since after six weeks the concentration of the stannous chloride was found to be practically unchanged. The outcome of the experiments go to prove that, although hydrogen sulphide appears to be evolved before sulphur dioxide, the evolution of hydrogen sulphide is due to previous solution of sulphur dioxide. In no case is stannous chloride completely oxidised by dilute sulphuric acid, and no oxidation occurs unless the solutions are warmed.

The following gives an idea of the influence of dilution on the final products of the reaction:

TABLE A.

	Molecular ratios.					
Expt.	$SnCl_2$.	HCl.	H_2SO_4.	H_2O.	Gas evolved.	Approximate temperature.
1	1	3·55	0·5	24	H_2S	boiling point.
2	1	3·55	2·0	24	H_2S	near boiling point.
3	1	3·55	4·0	24	H_2S	about 80°.
4	1	3·55	4·0	87	H_2S	after long boiling.
5	1	3·55	6·0	24	H_2S	about 70°.
6	1	3·55	10·0	24	H_2S then SO_2	about 30°.
7	1	3·55	10·0	87	H_2S	boiling point.
8	1	3·55	20·0	24	H_2S immediately followed by SO_2	gentle warming.
9	1	3·55	10·0	148	trace of H_2S	5 hours' boiling under a reflux.
10	1	—	5·0	29	H_2S	90 minutes' boiling under a reflux.
11	1	—	4·0	36	H_2S	75 minutes' boiling under a reflux.

In the last two experiments the amount of tin oxidised to the stannic state was 28·6 and 19·9 per cent. respectively. Crystals of stannous sulphate separated in the flask (No. 10) on cooling.

The Action of Stannous Chloride on Sulphurous Acid.

Several experiments (not cited) were made, in which sulphur dioxide was passed into stannous chloride solutions with and without hydrochloric acid. In all cases there was some oxidation of tin; precipitates occurred only when free hydrochloric acid was present in considerable excess. These precipitates consisted, for the most part, of stannic sulphide anl sulphur.

In order to obtain quantitative results, definite volumes of

standard solutions of sulphurous acid and of stannous chloride were mixed in 230 c.c. flasks, which were kept corked, and the contents were examined after definite intervals of time. In all cases the temperatures were noted; in the later experiments a thermostat was employed.

In the first series (table B) 5 c.c. of a stannous chloride solution containing 1·65 grams of stannous chloride, 1·1455 grams of hydrogen chloride, and 3·86 grams of water, were used for each experiment. The volume of sulphurous acid (1 c.c. = 0·032 gram H_2SO_3) was varied.

In the second series (table C) 5 c.c. of freshly prepared stannous chloride solution contained 0·271 gram of stannous chloride, and was normal as regards free hydrochloric acid. The sulphurous acid was more dilute (1 c.c. = 0·00348 gram H_2SO_3).

The eight estimations (table B) were made after three hours with $N/2$-permanganate, and the three estimations (table C) after twenty-two hours with $N/10$-permanganate. The results in table C are so expressed as to make them strictly comparable with those in table B, and results from final "*d*" series, for three and twenty-two hours, are inserted.

TABLE B.—Three hours at 15° (approx.).

1	2 Molecular ratios of ingredients				3	4	5	6	7	8
							c.c. $N/2$-$KMnO_4$. solution.			$SnCl_2$ oxidised per cent.
Expt.	i $SnCl_2$.	ii H_2SO_3.	iii HCl.	iv H_2O.	Description *p*=precipitate *c*=coloration.	Gas given off.	Expt.	Calc.	Diff.	
"*d*"	3	2·09	16·6	290	yellow skin	SO_2 (with thermostat 13°)				76·5
B i	3	0·278	10·85	110	pale brown *p*.	H_2S	21·7	28·3	−6·6	[17·9]
ii	3	0·556	10·85	150	buff brown *p*.	H_2S	16·4	21·9	−5·5	[37·8]
iii	3	0·937	10·85	210	yellow *p*. 0·1223 gram	H_2S	5·7	12·2	−6·5	[60·4]
iv	3	1·011	10·85	215	yellow *p*. 0·1173 gram	SO_2 faint	3·8	10·9	−7·1	[65·2]
v	3	1·084	10·85	225	yellow *p*. 0·1370 gram	SO_2	3·7	9·6	−5·9	[69·9]
vi	3	1·112	10·85	230	yellow *p*. 0·0984 gram	SO_2	3·7	9·0	−5·3	[71·2]
vii	3	2·085	10·85	360	pale yellow *p*. 0·0632 gram	SO_2	18·3	6·7	+11·6	66·6
viii	3	4·031	10·85	620	faint yellow *p*. sulphur only	SO_2	49·5	18·8	+30·7	11·6

TABLE C.—Twenty-two hours at 15° (approx.).

"*d*"	3	2·09	16·6	290	yellow skin	SO_2	(with thermostat 13°)			89·0
C *a*	3	6·0	10·35	600	faint yellow *c*.	SO_2	55·5	53·1	+2·4	93·0
b	3	2·25	10·35	380	faint yellow *c*.	SO_2	19·8	17·7	+2·1	93·9
c	3	1·0	10·35	240	faint yellow *c*.	none	4·5	11·6	−7·1	[64·5]
→	3	1·55	6·0	appear to be necessary for completing oxidation.						

In these tables the figures (column 2) in heavy type are given when the ratio $H_2SO_3/SnCl_2$ is greater than 1·55/3. In these cases the figures in column 7 are seen to be positive. Here the amount of permanganate (column 5) used is greater than the calculated amount (column 6), since, in the circumstances, the less the tin is oxidised by the sulphurous acid the greater is the amount of permanganate required.

In all other experiments a negative figure appears in column 7 which is fairly constant, the mean value being −6·3.

In B i and B ii a negative value might be anticipated since the brown precipitates, evidently containing stannous sulphide, were not subject to titration. The other negative values, however, were perplexing, as also was the fact, observed in the titration of these solutions, that after the pink tint was reached a further very slow degradation—through brown to milkiness—occurred. The figures (column 5) do not include such further additions of permanganate. The problem was solved by reference to Young's work (*loc. cit.*, first paper). He showed that a colloidal form of stannous sulphide is produced when hydrogen sulphide is employed as an accelerator in the oxidation of stannous chloride.

It seems, therefore, that in this case colloidal stannous sulphide is present during the titration, and accounts for the stage of slow action which follows the recorded titrations. The comparative constancy in the negative figures (column 7) shows that approximate equilibrium has been established in three hours. The percentages of tin oxidised in these cases therefore are calculated from the parallel figures under H_2SO_3, each being multiplied by 100/1·55. The figures are given in brackets, and must be regarded as only approximate because the ratio for calculation is not strictly 1·55/3 in these circumstances. As will be shown, the admixture should admit of complete oxidation for this to obtain.

The percentages of tin which had been converted into colloidal stannous sulphide have been calculated in all cases, and are found to be well within the limit imposed by the joint reactions:

$$\begin{cases} 3SnCl_2 + H_2SO_3 + 6HCl = 3SnCl_4 + 3H_2O + H_2S, \\ SnCl_2 + H_2S = SnS = 2HCl. \end{cases}$$

This limit is 25 per cent., and the maximum found (in B iv and C c) was 20·4 per cent. Referring to the oxidations in B vii and B viii: B vii indicates 10 per cent. less than appears on the "*d*" curve after three hours, but the greater dilution (360 to 290) and smaller excess of hydrogen chloride (4·85 to 10·6, after deducting 6) are both in keeping with the observed difference.

B viii indicates but slight oxidation, and its dilution (620) is the highest in the whole table.

In table C after twenty-two hours *a* and *b* appear to have reached an advanced stage of oxidation. Their excess over that of "*d*" may be due to their higher temperature, and to their larger excess of sulphurous acid, whilst their close proximity to each other might be surmised on referring to the figures under H_2SO_3 and H_2O (column 2), where excess of sulphurous acid would compensate for higher dilution.

The Formation of Sulphuric Acid during the Interaction of Stannous Chloride and Sulphurous Acid.

Qualitative experiments were made, in which stannous chloride and sulphurous acid were kept, together with hydrochloric acid, in closed flasks for one and a-half, four, and eighteen hours in an atmosphere of hydrogen. Each experiment was checked by a blank, in which stannous chloride was absent.

In every case there was evidence (reaction with barium chloride) that a small amount of sulphuric acid had been formed, and this formation was most evident in the experiment of longest duration. Quantitative experiments were made with the admixtures as used in the "*d*" experiments. In four cases the weight of stannous chloride taken was only 0·851 gram, and the oxidation, after twenty-four hours, had not reached completion.

In these cases the weights of barium sulphate were very small and not very concordant, but when ten times the weight of stannous chloride was submitted to oxidation for twenty-four hours at 18° (with a parallel blank experiment) complete oxidation was proved, and it was shown that 8·51 grams of stannous chloride yield sufficient sulphuric acid to produce 0·1239 gram of barium sulphate. Allowing for the slight precipitate in the blank experiment, it was found that just under 3 per cent. of the sulphurous acid employed in the whole oxidation was converted into sulphuric acid.

It was evident, therefore, that the reaction:

$$SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4$$

has taken place very slowly when compared with the oxidation of stannous chloride. It appears also that complete oxidation can only be brought about when there is an excess of sulphurous acid over and above what is required for the other reactions which occur.

Estimation of Sulphur and of Stannic Sulphide Precipitated in the Action, and its Bearing on the Calculations Made.

The estimation was also made with the "*d*" solutions. Nearly all the sulphur and stannic sulphide took the form of an easily

detached yellow skin, but a further small yellow deposit was induced by the addition of one or two drops of mercuric chloride solution.

When 0·851 gram of stannous chloride was treated, these precipitated skins were small, and the results not very concordant, but when 8·51 and 4·255 grams were taken the results agreed in showing that 48·4 of the extra fifty parts of sulphurous acid required for the second action:

(i) $3SnCl_2 + 6HCl + H_2SO_3 = 3SnCl_4 + 3H_2O + H_2S$,

(ii) $2H_2S + H_2SO_3 = 3H_2O + S$.

were eventually concerned in the production of free sulphur (when the H_2SO_3 in [i] is called 100).

The deposits were dried for twelve hours at 95°, and were weighed in a crucible which was then heated strongly.

In one case both sulphur and stannic sulphide were estimated independently; in the other case only the latter was estimated by conversion into stannic oxide. From these determinations it appeared that only 2·2 per cent. of the original stannous chloride was converted into stannic sulphide, according to the equation:

(iii) $2H_2S + SnCl_4 = 4HCl + SnS_2$;

and this result agrees with theory, for it is seen that if (ii) occurs to the extinction of (iii), then fifty parts of sulphurous acid should be required in (ii) for every 100 parts required in (i). Moreover, the weight of sulphurous acid in (i) will be supplemented only in as far as (ii) occurs, and, to a small extent, in as far as the reverse reaction:

(iv) $SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4$

takes place.

It has been assumed that 1·55 molecules of sulphurous acid are finally required for the complete oxidation of 3 molecules of stannous chloride. The figure is arrived at as follows:

For primary action (i) 100 parts being required;
Then for the reaction (ii) 48·4 parts are required;
And for the reaction (iii) 4·5 parts are required (= 3 per cent. × 1·5).

Since the 100 parts correspond with 1 molecule of sulphurous acid, the total, 152·9, corresponds with 1·529 molecules. In cases where no stannic sulphide appeared, there would be an addition of 0·016 of a molecule, making the total amount 1·545.

The figure 1·55 allows a small margin for oxidation by air. Strictly, a rather smaller figure should be used in calculations for the earlier stages (especially when stannous sulphide appears), and a rather larger one in the later stages when (iv) has become more

important. Nevertheless, the application of the mean value has explained nearly all the phenomena recorded.

Rate of Oxidation of Stannous Chloride by Sulphurous Acid.

Each experiment was conducted in a separate flask, holding approximately 230 c.c. Five c.c. of mixed stannous chloride–hydrochloric acid solution were introduced, and then 5 c.c. of the sulphurous acid solution were added, the time being noted. The flask was corked, shaken, and immediately placed in a thermostat (except in the "*a*" series). In cases of very short periods of action the exact temperature was obtained separately for each solution before admixture, and at the moment of expiry the contents of the flask were diluted rapidly and immediately titrated.

Before starting any series of experiments, 5 c.c. of each solution were independently titrated by the same permanganate solution. The final titration was always less than the sum of the above, and on multiplying the deficit by $3/(3+1{\cdot}55)$ the weight of oxidised stannous chloride was obtained in terms of permanganate.

The results are given in tables (*a*, *a'*, *b*, *c*, *d*). In each case the actual weights employed are stated. The figures given for water are deduced approximately from the specific gravities of the solutions.

TABLE *a*.

	Weight	Mol. ratio.
$SnCl_2$	0·2142	3·0
H_2SO_3	0·06724	2·18
HCl	0·182	13·3
H_2O	9·5	1200·0

Time.	Per cent. oxidised.
2 mins.	3·08
30 ,,	28·2
60 ,,	55·6
1·5 hours	68·1
2·0 ,,	75·2
3·5 ,,	80·5
6·6 ,,	86·8
6·6 ,,	86·6

Observations.

Temperature 15–16°. No precipitates, but yellow tint after six hours.
Experiments with new solutions.

TABLE *a'*.

	Weight.	Mol. ratio.
$SnCl_2$	0·2119	3·0
H_2SO_3	0·059	1·94
HCl	0·182	13·45
H_2O	9·5	1200·0

Time.	Per cent. oxidised.
10 mins.	49·2
20 ,,	55·6
30 ,,	53·6
60 ,,	67·5
[2·5 hours	75·1]
3·5 ,,	74·8
6·0 ,,	76·1
7·0 ,,	77·9

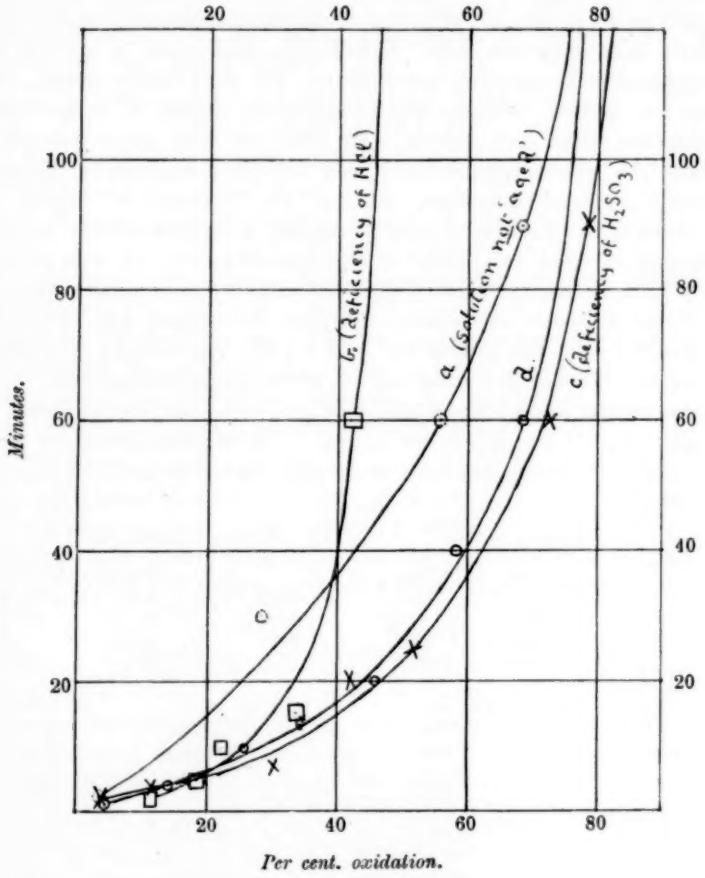
Observations.

Temperature 13°. No precipitates and no yellow tint in any case.
Experiments with week-old solutions.

The discrepancies between *a* and *a'* appeared to be inexplicable until the work of Young (*loc. cit.*) had been consulted. He showed that the rate of oxidation of stannous chloride increases with the

age of the solution. Referring to *a* and *a'*, it is seen that stannous chloride, when freshly prepared in admixture with hydrochloric acid, suffered an oxidation of only about 30 per cent in half-an-

FIG. 1.



hour, whereas with the week-old solution about 50 per cent. was oxidised in ten minutes, notwithstanding the lower temperature.

In the following series the stannous chloride–hydrochloric acid solutions were "aged" for at least a day before they were used.

TABLE *b*.

	Weight.	Mol. ratios.
$SnCl_2$	0·851	3·0
H_2SO_3	0·133	1·09
HCl	0·182	3·32
H_2O	9·5	300·0

Time.	Per cent. oxidised.	Time.	Per cent. oxidised.
2 mins.	11·0	15 hours	53·2
5 ,,	18·4	20·3 ,,	55·9
10 ,,	22·4	24·5 ,,	56·6
15 ,,	33·8	29·0 ,,	57·4
15 ,,	33·8		
60 ,,	41·8	after boiling*	77·2

Observations.

Temperature (first 6) 13°.
Temperature (last 4) 11°.
No precipitates.
Faint yellow tint after 15 hours.

* Last value (77·2) independent of factor otherwise used.

Here the concentration of stannous chloride was four times as great as in *a* and *a'*, but the hydrogen chloride and sulphurous acid were both in deficiency.

As eventually shown, the molecular rations:

$$SnCl_2 : H_2SO_3 : HCl$$

should have been 3 : 1·55 : 6, but here they were 3 : 1·09 : 3·32.

In these circumstances it was impossible to reach complete oxidation even if stannic hydroxide took the place of stannic chloride.

TABLE *c*.

	Weight.	Mol. ratio.
$SnCl_2$	0·851	3·0
H_2SO_3	0·133	1·09
HCl	1·09	20·0
H_2O	14·5	450·0

Time.	Per cent. oxidised.
1·5 mins.	3·34
4 ,,	12·1
4 ,,	10·1
7 ,,	30·5
20 ,,	44·0
25 ,,	51·5
60 ,,	72·4
1·5 hours	78·8
3 ,,	80·5

Observations.

Temperature 11°
Yellow precipitates appeared in less than a minute.

TABLE *d*.

	Weight.	Mol. ratio.
$SnCl_2$	0·851	3·0
H_2SO_3	0·25	2·09
HCl	0·9	16·6
H_2O	9·0	290·0

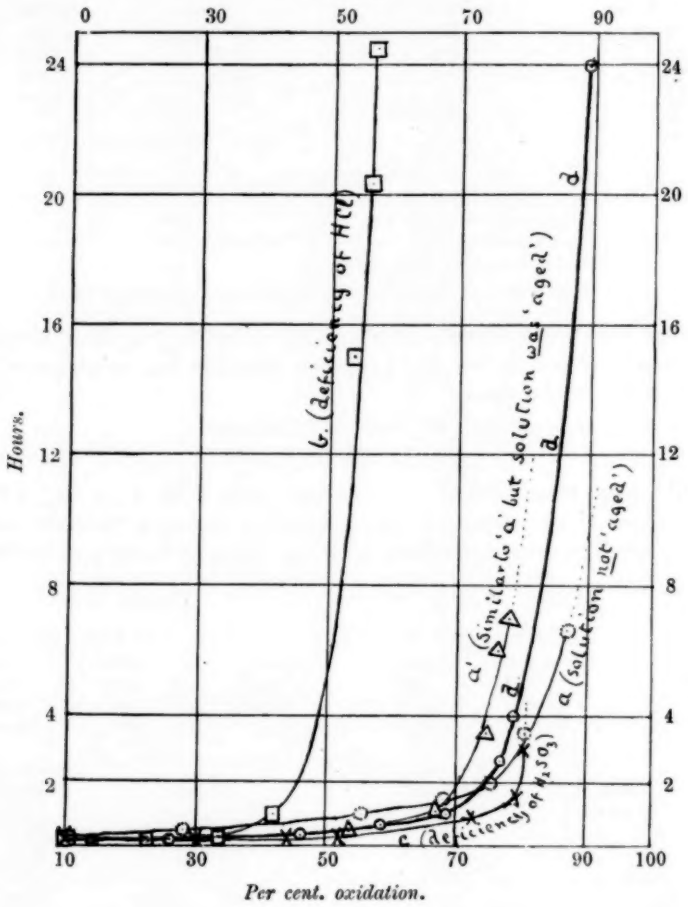
Time.	Per cent. oxidised.
1 mins.	4·66
4 ,,	14·1
10 ,,	25·9
20 ,,	46·3
40 ,,	58·3
60 ,,	68·5
2·6 hours	76·6
4 ,,	78·2
24 ,,	89·8

Observations.

Temperature 13°.
Yellow precipitates formed rapidly, soon taking the form of skins.

Comparing experiments *c* and *d*, the solution in the former contained an excess of hydrochloric acid and a deficit of sulphurous acid. These two factors tend to counterbalance each other, but on the whole the former solution was more rapidly oxidised. In *d* all the conditions for continued action were fulfilled; for this reason

FIG. 2.



and because the analyses were made (subsequently) with *d* solutions, the *d* curve is regarded as the most trustworthy.

Fig. 1 illustrates the progress of oxidation of stannous chloride during the first two hours. Fig. 2, on the same scale, includes nearly all the experiments, and illustrates the effects during the later stages of oxidation.

The letters (*a*, *a'*, *b*, *c*, *d*) refer to the foregoing tables respectively. The points specially brought out are:

(i) The comparatively slow oxidation of the freshly prepared stannous chloride–hydrochloric acid solution in "*a*" during the earlier stages; the "*a'*" solution follows the general trend, and differs from "*a*" in being a week old.

(ii) The slow oxidation in "*b*," due chiefly to a deficit of hydrogen chloride.

(iii) The tendency in "*c*" for the oxidation to come to a somewhat abrupt conclusion (compare also the negative figures in column 7, tables B and C), due to a deficit of sulphurous acid.

(iv) The similar character of "*c*" and "*d*" up to 70 per cent. of substance oxidised; in both cases there was a large excess of hydrochloric acid, greater in "*c*" than in "*d*."

The General Type of this Reaction.

If the reaction $H_2S + SnCl_2 = SnS + 2HCl$ is excluded, since it appears to be transient, there remain:

(i) $3SnCl_2 + H_2SO_3 + 6HCl = 3SnCl_4 + 3H_2O + H_2S$, which is the primary reaction;

(ii) $2H_2S + H_2SO_3 = 3H_2O + 3S$; and

(iii) $2H_2S + SnCl_4 = 4HCl + SnS_2$, which are secondary reactions.

(iv) $SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4$, which retards the oxidation, and results in the permanent production of sulphuric acid.

Of these the last has been shown to be very much slower than the rest; for the first 10 per cent. of substance oxidised it is calculated to be at least ten thousand times as slow as the oxidation during that early period.

If reaction (iv) predominates, the reaction should be of the third order, but a bimolecular reaction is indicated by the following figures deduced from the curves:

Apparent Values for K *in the Process of Oxidising Stannous Chloride by means of Sulphurous Acid.*

$SnCl_2$ oxidised. Per cent.	Termolecular values $K \times 10^6$				Bimolecular values $K \times 10^4$			
	a.	*b.*	*c.*	*d.*	*a.*	*b.*	*c.*	*d.*
10	1·67	6·17	2·93	3·35	1·57	5·85	2·77	3·96
20	1·65	1·76	4·68	4·02	1·47	1·56	4·17	4·17
30	1·93	2·37	5·21	4·37	1·58	1·95	4·29	4·01
40	2·34	1·94	5·55	5·55	1·75	1·39	4·17	4·04
50	2·89	0·33	5·46	6·62	1·92	0·22	3·60	3·99
60	3·75	—	6·25	6·56	2·21	—	3·57	3·62
70	5·26	—	7·75	7·02	2·43	—	3·59	3·40
80	6·66	—	—	4·09	2·22	—	2·28	1·40
90	—	—	—	3·11	—	—	—	0·63

The *b* series, in which there is a deficit of hydrogen chloride, may be dismissed. If the values from 20 to 70 per cent. in the other series are examined, the following appears:

Termolecular values.	*a*.	*c*.	*d*.
(*m*) Mean	2.97	5·81	5·79
(*n*) Max. difference	3·61	3·07	3·00
m/*n*.....	0·82	1·90	1·93
Bimolecular values.	*a*.	*c*.	*d*.
(*m*) Mean	1·89	3·90	3·89
(*n*) Max. difference	0·96	0·70	0·77
m/*n*.....	1·98	5·57	5·05

It is seen that the termolecular values for *a*, *c*, and *d* increase fairly steadily from 10 to 70 per cent., and the ratio *m*/*n* from 20 to 70 per cent. does not exceed 2, but with the bimolecular values, except for *a*, the figures do not rise progressively, whilst the ratio *m*/*n* is much more satisfactory.

In the case of *d* the bimolecular figures from 10 to 50 per cent. are satisfactory, and point to a reaction so far conforming closely to one of the second order. The experimental results, without smoothing, will stand examination fairly well for the first hour of action.

t= minutes.	*x*= per cent. oxidised.	$K \times 10^4$
1	4·66	4·88
4	14·1	4·10
10	25·9	3·49
20	46·3	4·31
40	58·3	3·49
60	68·5	3·59
	Mean value.....	3·98
	Max. difference	1·39

There is a correction which strictly should be applied to all these values of *K*. It has been tried in the case of "*d*," but does not alter the deduction that a bimolecular type predominates.

The Nature of Reactions involving Oxidation of Stannous Chloride.

Noyes (*loc. cit.*), noticing the tendency of hydrochloric acid to bring about an approximation to the second order in the oxidation by ferric chloride, stated that he was not then in a position to determine the exact nature of the rôle played by the acid.

Young (*loc. cit.*), in considering the kinetics of the action of oxygen on stannous chloride, points out that hydrogen chloride takes part in the first stages, and is a product in the latter stages. His conclusion is that dx/dt may reach a maximum in such reactions.

These conditions were fulfilled in the present instance. Hydrogen chloride takes part in the primary action, and is a product in the retarding action:

$$SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4.$$

High concentration of hydrochloric acid must decrease hydrolytic dissociation of stannous chloride, whilst the acid, although some of it takes part in the reaction, will suffer but small change in concentration. It may be for these reasons that the type approaches one of the second order.

Summary.

I. The action of concentrated sulphuric acid in excess on hydrated stannous chloride takes place in three successive stages:

(i) dehydration occurs at once;

(ii) liberation of hydrogen chloride between 20° and 90°;

(iii) liberation of sulphur dioxide between 130° and 200° with the formation of stannic sulphate according to the reaction:

$$SnSO_4 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O + SO_2.$$

Incidentally, stannous sulphate, when heated alone, liberates sulphur dioxide between 360° and dull red heat temperature in the reaction:

$$SnSO_4 = SnO_2 + SO_2.$$

When sulphuric acid acts on stannous chloride in the presence of water, various reactions occur, but these are due to secondary causes, namely, the influence of dissolved sulphur dioxide and hydrogen chloride.

II. The action of sulphurous acid on solutions of stannous chloride occurs at room temperatures, and varies according to the proportions of stannous chloride, sulphurous acid, hydrochloric acid, and water, which are in contact. The result is partial or complete oxidation of stannous chloride.

The oxidation is slow and incomplete unless there is excess of hydrochloric acid.

Direct evidence is forthcoming that five reactions are involved:

(1) Primary ..... $3SnCl_2 + 6HCl + H_2SO_3 = 3SnCl_4 + 3H_2O + H_2S.$
(2) Consequent... $2H_2S + H_2SO_3 = 3H_2O + 3S.$
(3) Consequent... $2H_2S + SnCl_4 = 4HCl + SnS_2.$
(4) Consequent... $H_2S + SnCl_2 = 2HCl + SnS.$
(5) Retarding ... $SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4$

Reaction (2) occurs to a greater extent than is the case with all the others except the primary.

Reaction (3) is not manifest except at high concentration of hydrochloric acid.

Reaction (4) occurs in the earlier stages; stannous sulphide

appears only when sulphurous acid is in defect, but there is evidence that a colloidal form is produced.

Reaction (5) occurs to a much smaller extent than the rest.

For complete oxidation it appears that the molecular ratios $SnCl_2 : H_2SO_3 : HCl$ must be in the proportion $3 : 1{\cdot}55 : 6$, approximately at least; higher proportions of sulphurous acid, and especially of hydrochloric acid, accelerate the oxidation.

The type of action is bimolecular provided that hydrochloric acid is in excess.

THE COLLEGE,
MARLBOROUGH.

[*Received, January 15th*, 1915.]

LXV.—*Studies on the Walden Inversion. Part I. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid.*

By GEORGE SENTER and HARRY DUGALD KEITH DREW.

THE remarkable phenomenon now so well known under the name of the Walden inversion may be illustrated by means of the following reactions discovered by Walden himself (*Ber.*, 1896, **29**, 133):

$$l\text{-Malic acid} \xrightarrow{PCl_5} d\text{-chlorosuccinic acid} \xrightarrow{Ag_2O} d\text{-malic acid}$$

and

$$d\text{-Chlorosuccinic acid} \begin{cases} \xrightarrow{Ag_2O} d\text{-malic acid} \\ \xrightarrow{KOH} l\text{-malic acid.} \end{cases}$$

The feature common to these and other reactions in which changes of the type of the Walden inversion occur is that there are always two steps (separate reactions) in passing from one optically active form to the other, and in spite of the large amount of work which has been done on the subject there does not appear to be one instance in which the stage at which the inversion occurs has been definitely established.

The importance of kinetic investigations in elucidating problems of this nature was first pointed out by one of us, and it was shown, for instance, that the reactions of chloro-acids with alkali hydroxides and silver salts respectively, which in some cases give rise to optically active products of different sign, differ fundamentally

inasmuch as the change takes place between the chloro-acid (or the corresponding ion) and hydroxyl and silver ions respectively * (Senter, T., 1910, **97**, 362). On the basis of these results Biilmann (*Annalen*, 1912, **388**, 330) has put forward a theory of the Walden inversion which has given rise to considerable discussion (compare Frankland, T., 1913, **103**, 713).

In continuation of this work, we are now engaged on an investigation of the influence of the conditions on the reaction between ammonia and the ammonium salts of *d*- and *l*-phenylchloroacetic acids. The method adopted was to choose such solvents that a homogeneous solution of the ammonium salt and excess of ammonia was obtained. The solutions were placed in Jena-glass tubes, which were then sealed and kept at a constant temperature for definite intervals. The phenylaminoacetic acid was then separated in a pure condition as described below, dissolved in dilute hydrochloric acid (0·984*N*), and the rotation determined. It may be mentioned that phenylaminoacetic acid has been resolved by Fischer and Weichhold (*Ber.*, 1908, **41**, 1285); the pure active acids have the rotations $[\alpha]_D^{20} \pm 157{\cdot}8°$.

The chief solvents hitherto used by us are water and acetonitrile. For the first-named solvent we have confirmed the results of previous observers that the reaction is attended by considerable racemisation, and that the resulting phenylaminoacetic acid has the opposite sign to the phenylchloroacetic acid taken. With acetonitrile as solvent there is also considerable racemisation, but the resulting amino-acid has the same sign as the phenylchloroacetic acid taken. This result has been confirmed by starting both with *d*- and with *l*-phenylchloroacetic acid. So far as we are aware, this is the first occasion on which a product of different sign has been obtained simply by varying the solvent. The only results comparable in any way with the above are due to Holmberg (*J. pr. Chem.*, 1913, [ii], **88**, 590), who, in some experiments on the reaction

* In an important paper (*J. pr. Chem.*, 1913, [ii], **88**, 590) referred to later in another connexion (see above), Holmberg states that I have referred the great reactivity of silver salts with chloro-acids, as compared with alkalis, to the catalytic influence of silver haloids, and he ascribes to Biilmann (*loc. cit.*) the suggestion that the chloro-acids or their ions react in the one case with silver ions, in the other case with hydroxyl ions. This is quite erroneous. The catalytic influence of silver haloids was established in certain cases (Senter, T., 1910, **97**, 358), but it is nowhere suggested that this accounts for the greater reactivity of silver salts as compared with alkalis—in fact the two effects are of quite a different order. The view that the reacting components in the case of alkalis and silver salts are OH' and Ag' ions respectively was definitely put forward in the same paper on the basis of experiment (*loc. cit.*, p. 362) and adopted with full acknowledgment by Biilmann (*loc. cit.*, p. 337). G. S.

between the alkali salts of *l*-bromosuccinic acid and alkali xanthates, finds that the sign of the resulting xanthosuccinic acid depends on the initial concentration of the reacting substances.

It might be suggested that the different results with the two solvents are connected with the presence of ammonium hydroxide in aqueous solution, but a little consideration shows that this is highly improbable. In the first place, the greater part of the ammonia in concentrated aqueous solution is almost certainly present as NH_3 (compare Perman, T., 1903, **83**, 1178; Moore, *ibid.*, 1907, **91**, 1382), and it seems likely that the amino-acid is formed by the action of NH_3 on the ammonium phenylchloroacetate, the mandelic acid simultaneously formed resulting from the action of water and ammonium hydroxide on the ammonium salt. These considerations receive support from the fact that Fischer and Scheibler (*Ber.*, 1908, **41**, 892) obtained an amino-acid of the same sign by the action of aqueous ammonia and of liquid ammonia respectively on d-α-bromo*iso*valeric acid.

A remarkable fact in the experiments with acetonitrile as solvent is that the proportion of active phenylaminoacetic acid in the product is practically independent of the temperature at which the reaction is carried out, being almost the same at 9° and 52°. On the other hand, the amino-acid obtained from solutions in water and in methyl alcohol at 52° was quite inactive, whilst an acid of considerable activity was obtained from aqueous solution at 9° (p. 642).

The use of acetonitrile as solvent in the preparation of phenylaminoacetic acid has considerable advantages, as a yield of 80 per cent. can readily be obtained, and, the amino-acid being practically insoluble in acetonitrile, the bulk of the product can be obtained at once by filtering and washing with cold water. In aqueous ammonia, as is well known, a considerable proportion of mandelic acid is formed, and we find that in methyl alcohol the yield of amino-acid is greatly diminished by the simultaneous formation of phenylmethoxyacetic acid.

Experiments with other solvents and with other reactions in which a Walden inversion may occur are in progress, and the results will be discussed when further data are available. It may be said at once, however, that the results now communicated appear to indicate the participation of one or both of the solvents in the reaction.

Experimental.

(1) *Preparation of* d- *and* l-*Phenylchloroacetic Acids.*

r-Phenylchloroacetic acid was prepared from mandelic acid and phosphorus pentachloride as described by Bischoff and Walden

(*Annalen*, 1894, **279**, 122), and resolved by means of morphine according to McKenzie and Clough's method (T., 1908, **93**, 811). The resulting *l*-acid, after recrystallisation from light petroleum (b. p. 30—50°), contained Cl = 20·8 (Calc., Cl = 20·8 per cent.), melted sharply at 61°, and gave the following values for the rotation: $[\alpha]_D^{16} - 185°$ in benzene solution (3 per cent.) and $[\alpha]_D^{16} - 158°$ in chloroform solution (1·5 per cent.), as compared with the values −191° and −159·4° given by McKenzie and Clough for benzene and chloroform solutions respectively. Repeated recrystallisation from light petroleum had no effect on the magnitude of the rotation.

The *d*-acid also melted sharply at 61°, as compared with the value 60—61° given by McKenzie and Clough (*loc. cit.*), and the rotation had the value $[\alpha]_D^{16} - 185°$ in benzene solution (3 per cent.).

(2) *Action of Ammonia on* r-*Phenylchloroacetic Acid in Acetonitrile at* 18°.

r-Phenylchloroacetic acid (1 gram) was dissolved in 18 c.c. of acetonitrile, the solution saturated with dry ammonia gas, and kept in a sealed tube for fourteen days at room temperature. A mass of crystals consisting of phenylaminoacetic acid and ammonium chloride gradually formed in the tube. The solvent was then expelled by heating on a water-bath, the residue dissolved in dilute hydrochloric acid, and the solution extracted several times with ether to remove unchanged phenylchloroacetic acid. The aqueous solution was neutralised with ammonia, and evaporated to a small bulk, and the amino-acid was filtered off and washed with cold water. The yield was 80 per cent. of the theoretical.

(3) *Action of Ammonia on* d- *and on* l-*Phenylchloroacetic Acid in Acetonitrile at* 9°.

In each case 0·75 gram of the active acid in 15 c.c. of the solvent was used, the solutions were kept for twenty-one days at 9°, and the amino-acid extracted as described under (2). In the case of the *l*-acid the first crop (0·2 gram) gave $[\alpha]_D^{15} - 4·5°$, and the second crop (0·03 gram) gave $[\alpha]_D^{15} - 107°$. For the *d*-acid the first crop (0·2 gram) gave $[\alpha]_D^{15} + 6·5°$, and the second crop (0·02 gram) gave $[\alpha]_D^{15} + 127·5°$. These results are in accord with the statement of Fischer and Weichhold (*loc. cit.*) that the solubility of the active acids in water is double that of the inactive acid. As the specific rotation of the pure *d*-acid is +157·9°, the second crop must have contained about 80 per cent. of the active acid.

(4) *Action of Ammonia on l-Phenylchloroacetic Acid in Acetonitrile at 52°.*

As the proportion of the active amino-acid formed is so small, an experiment was made with a larger quantity of acid in order to obtain sufficient of the highly active amino-acid for analysis. Further, as separate experiments showed that the yield of active acid at 52° was almost the same as at 9°, the experiment was made at the former temperature. Four grams of the acid in 70 c.c. of acetonitrile were saturated with dry ammonia, and kept for twenty-four hours at 52°. In this case the precipitate was separated by filtration, washed with a little cold water to remove ammonium chloride, and dried. The product, which weighed 2·25 grams, was free from chlorine, and contained N = 9·4 (Calc., N = 9·3 per cent.).

The rotation determined in 0·984*N*-hydrochloric acid was as follows:

$l = 2$-dcm.; $c = 2{\cdot}887$ (grams in 100 c.c.); α_D^{15} $-0{\cdot}50°$; $[\alpha]_D^{15}$ $-8{\cdot}7°$.

A second crop of the amino-acid (0·2 gram), isolated from the filtrate, contained the theoretical percentage of nitrogen, and the rotation was as follows:

$l = 2$; $c = 1{\cdot}790$; α_D^{16} $-2{\cdot}40°$; $[\alpha]_D^{16}$ $-67°$.

(5) *Action of Ammonia on l-Phenylchloroacetic Acid in Water at 9°.*

l-Phenylchloroacetic acid (0·75 gram) was dissolved in 15 c.c. of water, the solution saturated with ammonia, kept for nineteen days at 9°, and the amino-acid then isolated as described under (1). The product contained N = 9·36 (Calc., N = 9·30 per cent.), and the rotation was as follows:

First crop (0·25 gram):

$l = 2$; $c = 1{\cdot}000$; α_D^{15} $+1{\cdot}67°$; $[\alpha]_D^{15}$ $+83{\cdot}5°$.

Second crop (0·02 gram):

$l = 2$; $c = 0{\cdot}166$; α_D^{15} $+0{\cdot}45°$; $[\alpha]_D^{16}$ $+135{\cdot}5°$.

In conclusion, we desire to thank Mr. Gerald H. Martin for valuable assistance.

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[*Received, April 6th,* 1915.]

LXVI.—*The Absorption Spectra of the Isomerides of Ammonium d-α-Bromocamphor-β-sulphonate.*

By John Edward Purvis.

The author has investigated the absorption spectra of the two isomerides of ammonium *d*-α-bromocamphor-β-sulphonate described by Pope and Read (T., 1914, **105**, 800) to see if there were any differences in their absorptive capacities. According to Stewart (T., 1907, **91**, 199, 1537), in regard to stereoisomeric substances, "the compound having the greater molecular rotation has the greater absorption, but that the rule does not hold in the case of structure isomerides."

The two isomerides exhibited the angular rotations, $[M]_{Hg\ 5461}$ 371° and $[M]_{Hg\ 5461}$ 176° respectively. At the same time mixtures of the two substances were also examined, the angular rotations of which were 358° and 307° respectively. The alcoholic solutions were examined in the usual way. The molybdenum–uranium spark was the source of light, and each solution was examined under similar conditions of thickness of solution and time exposure.

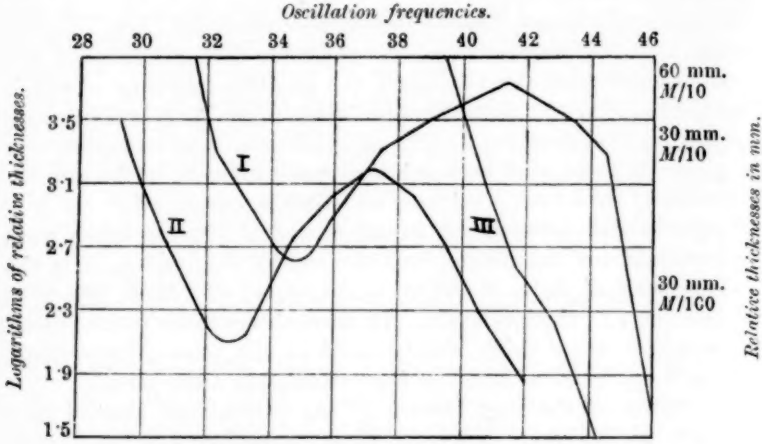
Equimolecular solutions of camphor and *d*-camphoroxime were also examined for comparison, and the results obtained confirm the previous work of Baly, Marsden, and Stewart (T., 1906, **89**, 979) and Hartley (T., 1908, **93**, 961). In these observations it was proved that camphor has a fairly strong band in the ultraviolet regions, whereas the oxime has none, and is remarkably transparent.

The results of the examination of the sulphonates showed that there was no difference either in their general or specific absorptions. The curve has been drawn, as well as the curves of camphor and camphoroxime (see Fig. I, II, and III). It will be noticed that the camphor band is much stronger and wider than that of the sulphonates, and there is also a greater shift, in the case of the heavier molecules of the latter, towards the red end. The transparency of the oxime is well shown by the line of general absorption (III).

The isomeric sulphonates, therefore, show no differences in their type of absorption, although they possess such striking differences in their angles of rotation. The latter may be considered to have their origin in the strains and stresses between a single (asymmetric) atom and the different groups of atoms with which it is connected, whereas specific and general absorption may be produced by oscillatory vibrations of an electronic nature set in motion by the radiant energy of the source of light. It is suggested that the CO-group in these substances is the primary oscillatory centre, and the suggestion is supported by the fact that camphoroxime has

no solution band, and is very transparent. Similar evidence is suggested by Hartley and Dobbie's observations (T., 1900, **77**, 318), where there was no selective absorption in solutions of acetaldoxime and acetoxime, although both acetaldehyde and acetone have strong absorption bands.

The observations of the author may also be cited (T., 1910, **97**, 3535; 1911, **99**, 107), which prove that when the oxygen of the carbonyl group in various coloured substances is replaced by other groups, the general line of absorption and the absorption bands are always shifted towards the more refrangible regions. In the same direction it may be recalled that chloral has a strong absorption band, whereas chloral hydrate has none, and is remarkably trans-



I. *Camphor.*
II. *Ammonium* d-*α-bromocamphor-β-sulphonate.*
III. d-*Camphoroxime.*

parent (Purvis and McCleland, T., 1912, **101**, 1810), and also the vapour of benzaldehyde has a considerable number of bands which are absent in the oxime (Purvis, T., 1914, **105**, 2482).

At the same time it should be understood that the final adjustment of the vibrations is influenced by the other atoms and atomic groups in the molecule. This is clearly indicated by the camphor band becoming narrower in the sulphonates, but the vibrations of the oscillatory systems of the latter substances must be similar, otherwise there would be differences in their absorptive capacities.

I desire to thank Professor Pope for the substances used in this investigation.

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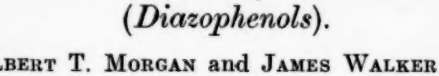
[*Received, April 8th*, 1915.]

LXVII.—*The Constitution of Internal Diazo-oxides (Diazophenols).*

By GILBERT T. MORGAN and JAMES WALKER PORTER.

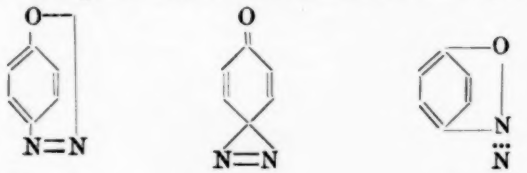
THE so-called diazophenols are in reality internal diazo-oxides (II) formed by a process of dehydration from the true diazophenols (I) which have not hitherto been isolated:



(I.) (II.)

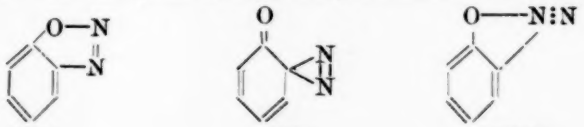
These diazo-oxides are compounds of great historic interest, inasmuch as the production by Griess of one member of the series from picramic acid led this investigator to undertake his classical researches on diazo-compounds (*Annalen*, 1858, **106**, 123; 1860, **113**, 201). More recently these substances have acquired considerable industrial importance owing to the circumstances that the ortho-diazo-oxides furnish azo-dyes capable of forming valuable lakes with chromic oxide, as, for example, Diamond Black P.V.

The constitution of these internal anhydrides of diazophenols has already received considerable attention, and although at first the compounds were given the *eso*-diazo-oxide formulæ (III and VI),



(III.) (IV.) (V.)

latterly the prevailing view has been that they are substances of quinonoid type (IV and VII). In a recent communication (*Ber.*, 1914, **47**, 1407) Klemenc advocates the diazonium formulæ (V and VIII) for these compounds, regarding them as internal salts:



(VI.) (VII.) (VIII.)

Klemenc's reasons for rejecting both the diazo-oxide and quinonediazide formulæ in favour of the diazonium structure are based on the following considerations.

The anhydrides of diazophenols resemble internal diazonium salts such as the sulphonates and carboxylates in the following respects:

(1) their extremely explosive character; (2) their sparing solubility in organic media; and (3) their formation in acid solutions.

(4) Klemenc does not consider that the pronounced colour of these anhydrides is an insuperable objection to their inclusion in the category of diazonium salts, which in the benzene series are usually colourless.

(5) The production of an internal diazonium sulphonate from nitrometanilic acid and the non-formation of a diazo-anhydride from *m*-aminophenol he regards as a minor difference, and due to the decomposable nature of the diazo-derivative of *m*-aminophenol.

In discussing the claims of the three rival formulæ it would be well to take Klemenc's determining factors in the order indicated above.

(1) *Extremely Explosive Character.*—Klemenc holds an exaggerated notion of the explosibility of "diazophenols." Estimations of nitrogen by the Dumas method were safely performed with three of these substances, including 2-nitrobenzene-4-diazo-1-oxide, which was considered by Klemenc to be too explosive for ultimate analysis by combustion.

Although these diazo-oxides explode vigorously when heated to their decomposing points, yet at the ordinary temperature they can be handled in the dry state with far greater security than is the case with internal diazonium sulphonates, such as "diazobenzenesulphonic acid," which have often given rise to serious accidents by detonating at the ordinary temperature even in a moist condition. In the case of nitrated diazo-oxides it may be added that the chief point of historic interest attaching to them is their comparatively high degree of stability, a property which enabled Griess (*loc. cit.*) to isolate 4:6-dinitrobenzene-2-diazo-oxide even while operating with nitrous and picramic acids in warm solution at 50° (compare Stenhouse, T., 1868, **6**, 150).

Sparing Solubility in Organic Media.—The nitrated diazo-oxides dissolve in ethyl acetate and the alcohols, but are not very appreciably soluble in non-hydroxylic or anhydrous solvents. This sparing solubility in organic media is probably due to the presence of nitro-groups, for the halogenated diazo-oxides described by Orton (T., 1903, **83**, 811; *Proc. Roy. Soc.*, 1903, **71**, 153) are readily soluble in the ordinary organic solvents with the exception of petroleum. These facts indicate that sparing solubility in organic media is not a general property of *eso*-diazo-oxides. On the other hand, these substances when dry are less readily soluble in water than many diazonium salts. It should, however, be noticed that in aqueous solution the hydrated diazophenols do not always readily assume the sparingly soluble anhydride form. The dehydration

process is probably in some instances retarded by the presence of excess of water (see p. 653).

(3) *Formation in Acid Solution.*—The first exception which can be taken to this consideration is that it is far from being the condition which generally obtains when *eso*-diazo-oxides are produced. Although halogenated and nitrated ortho- and para-aminophenols yield internal diazo-oxides in the presence of mineral acid this is not true of ortho- and para-aminophenols themselves (Hantzsch and Davidson, *Ber.*, 1896, **29**, 1522). These two substances yield diazonium salts in acid solutions, and the intervention of an alkali, such as sodium hydroxide or silver oxide, is required before internal condensation takes place.

Klemenc's belief that in acid solution the change from quinquevalent to tervalent diazo-nitrogen cannot occur is not supported by the general behaviour of aromatic diazonium salts. The facility with which this change takes place depends not only on the acidity of the solution, but also on the nature and orientation of the substituents in the aromatic nucleus. Negative substituents, such as halogen atoms or nitro-groups, increase this tendency; positive substituents, such as alkyl groups, render the quinquevalent condition more stable (Engler and Hantzsch, *Ber.*, 1900, **33**, 2148).

The unskilful diazotisation of aromatic amines frequently leads to the production of diazoamino-compounds even in acid solution. This is especially noticeable in the case of *p*-nitroaniline, yet so far from the product, 4 : 4′-dinitrodiazoaminobenzene, being a diazonium salt it is actually a weak acid forming intensely coloured alkali salts (Meldola and Streatfeild, T., 1886, **49**, 627).

The production of diazoamines and the formation of *eso*-diazo-oxides are comparable reactions, and when these processes occur in acid solution there is in all probability a preliminary change in diazo-nitrogen from the quinquevalent to the tervalent condition.

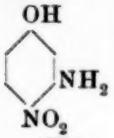
(4) *Colour of* eso-*Diazo-oxides.*—The internal anhydrides of the diazophenols have a pronounced yellow colour, a physical property which must be regarded as strong evidence in favour of the quinone-diazide constitution for these compounds. Klemenc's assertion that, as diazonium phenoxides, they should be at least as coloured as the salts of substituted phenols, does not carry conviction. Although the salts of nitrated phenols are coloured, those containing other substituents, such as halogen atoms or methyl or sulphonic groups, are colourless.

The internal diazonium sulphonates of the benzene series are colourless, whereas those of the naphthalene series are generally described as coloured substances.

In these two instances of the salts of substituted phenols and the

internal diazonium sulphonates, colour is not a general property, whereas it is in the case of all *eso*-diazo-oxides.

(5) *Non-existence of Internal* m-*Diazo-oxides.*—Inasmuch as the non-formation of benzene-3-diazo-oxide is assumed by Klemenc to be due to the instability of phenol-*m*-diazonium chloride, we have examined the following series of nitrated *m*-aminophenols first described by Meldola and Stephens (T., 1906, **89**, 924):



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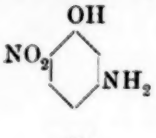
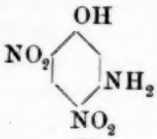


(X.)



(XI.)

These three compounds, which furnish diazonium salts of considerable stability, do not, however, yield internal *m*-diazo-oxides under experimental conditions similar to those leading to the production of ortho- and para-diazo-oxides from nitrated ortho- and para-aminophenols respectively. Our negative results confirm those of Hantzsch and Davidson (*loc. cit.*) working on the less stable phenol-*m*-diazonium salt. If condensation to form the diazo-oxide were entirely a matter of internal salt-formation between the strongly basic diazonium complex and the acidic hydroxyl group one would expect the dehydration to occur even when these groups have a meta-orientation to one another, especially in those cases where the acidity of the hydroxylic hydrogen is enhanced by the presence of a contiguous nitro-group, as in the nitrated *m*-aminophenols (X and XI).

Accordingly, we maintain that the non-existence of internal meta-diazo-oxides on the one hand, and on the other the well-established general formation of ortho-, para-, and peri-diazo-oxides from ortho-, para-, and peri-hydroxydiazonium salts respectively, warrants the rejection of the diazonium constitution for the internal diazo-oxides, this conclusion being supported by the contributory evidence set forth under the four preceding headings.

The arguments in favour of the quinonediazide and *eso*-diazo-oxide formulæ may be summarised as follows:

Quinonediazide Structure.—(1) The yellow colour of these internal diazo-anhydrides and their sensitiveness to light.

(2) The non-existence of internal meta-diazo-oxides.

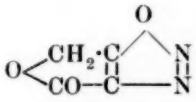
(3) The marked contrast between the reactivity of these diazo-anhydrides and the inertness of ortho-diazoimines and ortho-diazo-sulphides (Jacobsen, *Annalen*, 1893, **277**, 210).

(4) The remarkable difference in colour and other physical and chemical properties between these diazo-anhydrides and diazo-tetronic anhydride (Wolff, *Annalen*, 1900, **312**, 126).

Points 1 and 2 have already received attention. The ortho-diazoimines and ortho-diazosulphides, which are produced directly from ortho-diamines and ortho-aminothiophenols respectively without the intermediate formation of diazonium salts, are generally regarded as typical cyclic compounds arising entirely from the tendency for ring-formation. A comparison of their properties with those of the ortho-diazo-oxides certainly tends to exclude a cyclic constitution for the latter substances.

Cyclic Diazo-oxide Structure.—(1) The colour of the *eso*-diazo-oxides is not incompatible with the presence in their molecules of the group $-N{:}N\cdot O-$, for this group is also present in the coloured diazo-oxides $R\cdot N{:}N\cdot O\cdot R'$ prepared by coupling the diazonium salts $R\cdot N_2Cl$ with the phenols $R'\cdot OH$.

(2) In spite of differences of colour, the diazo-complex in the *eso*-diazo-oxides may have the same structure as in Wolff's diazotetronic anhydride (XII):



(XII.)

(XIII.)

It is generally urged that since this non-aromatic diazo-anhydride, for which a cyclic structure is assumed, is colourless, therefore a cyclic constitution for the diazo-oxide complex in the anhydro-diazophenols is inadmissible.

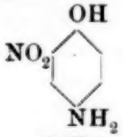
Attention may be directed to the analogous difference observed between yellow diazoaminobenzene, $C_6H_5\cdot N_2\cdot NH\cdot C_6H_5$, and colourless diazoaminomethane, $CH_3\cdot N_2\cdot NH\cdot CH_3$ (Dimroth, *Ber.*, 1905, **38**, 1575; 1906, **39**, 3909). Although both substances are generally considered to contain the same diazoamino-grouping, $-N{:}N\cdot NH-$, the lack of colour in the latter case is attributed to the absence of aromatic nuclei which are present in diazoaminobenzene to form with the diazoamino-group a chromogenic complex. So also in the case of diazotetronic anhydride the lack of colour is similarly attributable to the absence of aromatic nuclei, and not to any difference between the $-N_2\cdot O-$ group present in this compound and that contained in the coloured aromatic *eso*-diazo-oxides.

(3) The existence of peri-diazo-oxides (XIII) obtained from 8-amino-α-naphthol and its derivatives (D.R.-P. 55404, 62289, 81282, 82900), comparable in their physical and chemical properties with the ortho- and para-diazo-oxides, renders the quinonediazide configuration generally inapplicable, inasmuch as these peri-diazo-oxides cannot be formulated as quinonediazides without making unwarranted assumptions in regard to the linking up of carbon

atoms in the naphthalene residue (Morgan and Micklethwait, T., 1908, **93**, 607).

This survey of the existing evidence shows that the quinonediazide formulation (formulæ IV and VII), although not entirely excluded, is less generally serviceable than the cyclic diazo-oxide structure (formulæ III and VI). The two views represented by these two sets of formulæ are not irreconcilable if it be remembered that the diazo-oxide structure corresponds with the peroxide phase of ortho- and para-quinone configuration, and has the additional advantage of being applicable to the case of the peri-diazo-oxides in which the quinonediazide phase is in all probability almost entirely suppressed.

In the experiments described below a comparative study has been made of the formation of diazo-oxides from the following nitro-aminophenols: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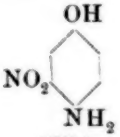
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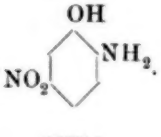
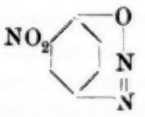

(XVI.)

Of these three compounds 3-nitro-4-aminophenol (XV) yields its diazo-oxide (XVIII) with least facility. This product is not obtained even on neutralising the acid solution of diazonium salt with sodium hydrogen carbonate; it is best prepared by treating 3-nitro-4-aminophenol with nitrous fumes in ethereal solution: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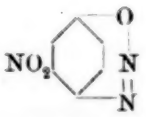
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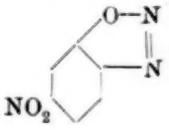
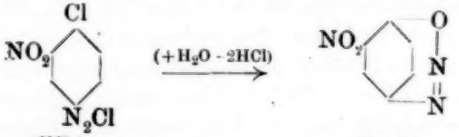

(XIX.)

5-Nitro-2-aminophenol (XVI) and 2-nitro-4-aminophenol (XIV) both yield their respective diazo-oxides (XIX and XVII) in acid solutions.

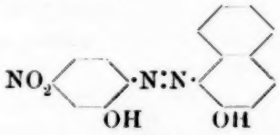
2-Nitrobenzene-4-diazo-1-oxide (XVII) was also obtained quantitatively by the hydrolysis even in acid solutions of 4-chloro-3-nitrobenzenediazonium chloride (XX), a method of preparation com-


(XX.) (XXI.)

parable with Klemenc's production of this diazo-oxide from

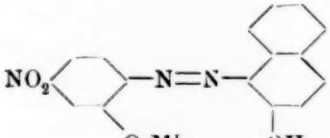
4-methoxy-3-nitrobenzenediazonium chloride. It is therefore evident that in this case the tendency to form the diazo-oxide is very pronounced.*

The foregoing diazo-oxides were characterised by conversion into the azo-β-naphthol derivatives; one of these, namely, 4-*nitro*-2-*hydroxybenzeneazo*-β-*naphthol*,



(XXII.)

gives rise to intensely coloured metallic salts, in which the metal probably replaces the hydrogen of the benzenoid hydroxyl and co-ordinates with the naphthalenoid hydroxyl, the development of the intense colour being due to the formation of a cyclic lake complex,



(XXIII.)

A similar structure probably exists in the chrome-developed Diamond Black P.V. and other members of this series of mordant dyes.

Experimental.†

2-*Nitrobenzene*-4-*diazo*-1-*oxide* (XVII).

Two methods of preparation were employed in the case of this diazo-oxide, the starting points being respectively *m*-nitroaniline and *p*-chloroaniline.

(1) *Preparation from* m-*Nitroaniline.*—This nitro-base was diazotised and converted by the addition of sodium azide into 3-nitrophenylazoimide. The triazo-derivative was cautiously heated on the water-bath with sulphuric acid (2 vols. H_2SO_4 : 1 vol. H_2O), when nitrogen was eliminated and the sparingly soluble sulphate of 2-nitro-4-aminophenol crystallised on cooling, the product being freed from small amounts of 4-nitro-2-aminophenol sulphate by

* In describing this formation of a diazo-oxide by the demethylation of a nitroanisidine derivative, Klemenc makes no reference to the fact that this reaction was first discovered by Meldola and Stephens (T., 1905, **87**, 1205).

† The earlier experiments in this investigation were carried out by Corporal J. C. Elliott, R.E., for whose help we desire to express our indebtedness.

crystallisation from water (Friedländer and Zeitlin, *Ber.*, 1894, **27**, 192).

The addition of aqueous sodium nitrite to a solution of 2-nitro-4-aminophenol sulphate in ice-cold dilute sulphuric acid determined the formation of a yellow, crystalline precipitate of 2-nitrobenzene-4-diazo-1-oxide, which separated completely even in presence of excess of mineral acid. The diazo-oxide was crystallised from hot water, and separated in yellow leaflets; it exploded with considerable violence at 168°:

0·1240 gave 28 c.c. N_2 at 18° and 760 mm. N = 26·09.

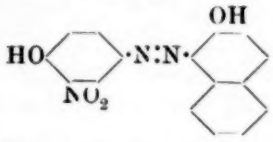
$C_6H_3O_3N_3$ requires N = 25·45 per cent.

2-Nitrobenzene-4-diazo-1-oxide was moderately soluble in acetone and ethyl acetate, sparingly so in methyl and ethyl alcohols, and insoluble in benzene and chloroform. Prolonged boiling with the alcohols led to the production of *o*-nitrophenol. The diazo-oxide coupled readily with alkaline β-naphthol to a red azo-derivative, which crystallised from ethyl acetate in orange-red leaflets, and melted at 216°:

0·0610 gave 7·4 c.c. N_2 at 18° and 738 mm. N = 13·60.*

$C_{16}H_{11}O_4N_3$ requires N = 13·59 per cent.

3-*Nitro-4-hydroxybenzeneazo-β-naphthol*,



was readily soluble in benzene, and sparingly so in alcohol or glacial acetic acid; it dissolved in cold concentrated sulphuric acid to a crimson solution. The alkali salts were soluble in water to a deep crimson solution.

(2) *Preparation from* p-*Chloroaniline*.—The chloro-base was dissolved in 10 parts of cold concentrated sulphuric acid, the solution cooled to 0°, and treated with rather more than the calculated amount of nitric acid (D 1·52) mixed with 10 parts of concentrated sulphuric acid. The solution was poured on to ice, partly neutralised with sodium carbonate, and the precipitated 4-chloro-3-nitroaniline crystallised from boiling water. By operating with nitric acid freed from nitrous fumes and working at low temperatures the yield of 4-chloro-3-nitroaniline was rendered nearly quantitative (compare Claus and Stiebel, *Ber.*, 1887, **20**, 1380).

The diazotisation of 4-chloro-3-nitroaniline in moderately concen-

* In this and the foregoing estimation the nitrogen was collected over water, in the remaining determinations it was collected over 50 per cent. potassium hydroxide.

trated hydrochloric or sulphuric acid led to the production of 4-chloro-3-nitrobenzenediazonium chloride or sulphate. Either of these salts was precipitated in a colourless, crystalline form by adding alcohol and ether to the aqueous acid solution. When, however, the acidity of the diazo-solution was diminished by dilution, partial neutralisation, or the addition of sodium acetate the liquid became yellow, and 2-nitrobenzene-4-diazo-1-oxide separated quantitatively in yellow leaflets. The product was identical with the preceding preparation; it exploded violently at 168°, and coupled with alkaline β-naphthol, yielding the azo-derivative melting at 216°. 2-Nitrobenzene-4-diazo-1-oxide coupled with alkaline resorcinol, forming an orange azo-derivative soluble in aqueous alkali hydroxides to a deep red solution. The azo-compound with tolylene-2:4-diamine was brown, turning orange-red with dilute acids; it dissolves in aqueous potassium hydroxide to a deep orange-red solution, and gave a crimson coloration, fading to orange-red with concentrated sulphuric acid.

2-Nitrobenzene-4-diazo-1-oxide did not couple readily with alcoholic β-naphthylamine, but when added to a solution of this base in dilute acetic acid there was a well-marked time reaction, the red azo-derivative separating completely after three or four minutes. This azo-compound, which crystallised from benzene in bright red needles melting at 226°, was soluble in aqueous alkali hydroxides to a brownish-red solution, and developed with concentrated sulphuric acid a deep blue coloration fading to yellow.

3-*Nitrobenzene*-4-*diazo*-1-*oxide* (XVIII).

o-Nitroaniline was successively diazotised and converted into 2-nitrophenylazoimide. This triazo-derivative was gently heated on the water-bath with five parts of moderately concentrated sulphuric acid (2 vols. H_2SO_4 : 1 vol. H_2O) until after one hour it had all dissolved (Friedländer and Zeitlin, *loc. cit.*). The acid solution diluted with water and partly neutralised with sodium hydrogen carbonate yielded a precipitate of 3-nitro-4-aminophenol, which was purified by crystallisation from water containing animal charcoal and from benzene. The compound formed a hydrate which crystallised from water or benzene in dark red needles with green metallic reflex; it melted at 81—85°, and when dried in the steam-oven it changed to a brownish-red powder of the anhydrous substance melting at 144°.

The diazotisation of 3-nitro-4-aminophenol in hydrochloric acid solution, followed by the addition of sodium acetate or sodium hydrogen carbonate, did not determine the precipitation of the corresponding diazo-oxide, which, however, was obtained by the following methods:

(i) 3-Nitro-4-aminophenol (0·5 gram) was dissolved on warming in 1 c.c. of glacial acetic acid and 5 c.c. of water. The cooled solution yielded a mass of feathery crystals, to which was added excess of ethyl nitrite (1·5 c.c.). The crystals dissolved, a slight flocculent residue was removed, the filtrate concentrated to half its volume in a vacuum desiccator, some tarry matter was separated, and the evaporation continued to dryness, when *3-nitrobenzene-4-diazo-1-oxide* was obtained in clusters of brown needles. The product, which at first was resinous, became quite friable on digestion with cold water, in which it was then sparingly soluble. When hydrochloric acid was used in this experiment instead of acetic acid no diazo-oxide was obtained; the diazonium chloride remained unchanged after two days in the vacuum desiccator over solid potassium hydroxide.

(ii) 3-Nitro-4-aminophenol (0·5 gram) was dissolved in ether (20 c.c.) and alcohol (6 c.c.), and the well-cooled solution treated with nitrous fumes from nitric acid and arsenious oxide. 3-Nitrobenzene-4-diazo-1-oxide separated as a brown, crystalline deposit, which was washed with ether and dried under diminished pressure:

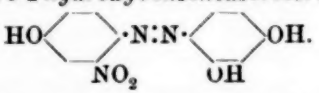
0·0784 gave 17·3 c.c. N_2 at 17° and 734 mm. N = 25·20.

$C_6H_3O_3N_3$ requires N = 25·45 per cent.

3-Nitrobenzene-4-diazo-1-oxide exploded with moderate violence at 119°; it dissolved readily in warm water to a pale yellow solution; it was fairly soluble in ethyl acetate, acetone, or absolute alcohol, separating from the first solvent in well-defined, brown needles, and from the other two in small, acicular crystals. It was almost insoluble in dry ether, and only sparingly soluble in benzene.

When added to aqueous resorcinol the diazo-oxide did not couple, but this reaction occurred immediately on adding a trace of alkali, which acted catalytically.

2-Nitro-4-hydroxybenzeneazoresorcinol,



This azo-derivative, which was prepared by coupling alkaline resorcinol either with the preceding diazo-oxide or with 2-nitro-4-hydroxybenzenediazonium chloride, separated from alcohol in brownish-red crystals, melting and decomposing at 212°:

0·0893 gave 11·6 c.c. N_2 at 15° and 745 mm. N = 15·17.

$C_{12}H_9O_5N_3$ requires N = 15·27 per cent.

The azo-resorcinol developed a permanent brownish-red colora-

tion with concentrated sulphuric acid. 3-Nitrobenzene-4-diazo-1-oxide did not couple readily with alkaline β-naphthol, and as the brownish-purple azo-derivative when prepared from 2-nitro-4-hydroxybenzenediazonium chloride was somewhat tarry, it was not further examined.

5-*Nitrobenzene*-2-*diazo*-1-*oxide* (XIX).

p-Nitroaniline was converted into 4-nitrophenylazoimide, and this substance heated cautiously with five parts of sulphuric acid (1 vol. H_2SO_4 : $2H_2O$) on the water-bath. The mixture was warmed and shaken until the triazo-derivative had dissolved; this required three to four hours, as the decomposition was effected with as little warming as possible to avoid the formation of tar. The brown solution was diluted, and gradually neutralised with sodium hydrogen carbonate. The first precipitate, being tarry, was removed; the subsequent brown, flocculent precipitate was washed, dissolved in hot water, boiled with animal charcoal, and the filtered solution on cooling deposited glistening, brown needles of 5-nitro-2-aminophenol (m. p. 199°). This aminophenol (1 gram) dissolved in water (18 c.c.) and hydrochloric acid (3 c.c.) was treated slowly at 0° with 10 c.c. of aqueous sodium nitrite (5 per cent.), when the diazo-oxide separated in acicular crystals. From solutions containing a larger proportion of mineral acid the diazo-oxide separated in garnet-red prisms after partial neutralisation with sodium hydrogen carbonate.

5-*Nitrobenzene*-2-*diazo*-1-*oxide* was also prepared by adding ethyl nitrite to a glacial acetic acid solution of 5-nitro-2-aminophenol and evaporating the solution under diminished pressure. On heating, this diazo-oxide darkened at 95°, became black at 105°, and exploded with extreme violence at 111°. In one instance the melting-point tube was projected through the bottom of the sulphuric acid bulb. Nevertheless, the compound burnt quietly with copper oxide:

0·0600 gave 13·2 c.c. N_2 at 14° and 745 mm. N = 25·77.

$C_6H_3O_3N_3$ requires N = 25·45 per cent.

5-Nitrobenzene-2-diazo-1-oxide dissolved only sparingly in ether or benzene; it was fairly soluble in hot water or alcohol to a yellow solution. From its orange-red solution in acetone or ethyl acetate it separated on spontaneous evaporation in lustrous red needles.

4-*Nitro*-2-*hydroxybenzeneazo*-β-*naphthol* (XXII) was obtained in the form of its dark blue alkali salt by adding the preceding diazo-oxide to β-naphthol (1 mol.) dissolved in 2*N*-potassium hydroxide when the sparingly soluble potassium salt separated. This product was washed with water, and acidified to liberate the bright red

azo-derivative, the latter being purified by dissolving in alcohol and precipitating by addition of water:

0·1110 gave 11·8 c.c. N_2 at 12° and 755 mm. N = 12·71.

$C_{16}H_{11}O_4N_3$ requires N = 13·59 per cent.

4-Nitro-2-hydroxybenzeneazo-β-naphthol, which was not a very crystallisable compound, was readily soluble in ethyl acetate, alcohol, or acetic acid, and sparingly so in benzene or chloroform. When dry the azo-compound was brownish-red, and developed with concentrated sulphuric acid an intense purple coloration fading to yellow.

The *monopotassium* salt (XXIII) of 4-nitro-2-hydroxybenzeneazo-β-naphthol was conveniently prepared by dissolving the generating diazo-oxide in alcoholic β-naphthol, and then slowly adding 2*N*-potassium hydroxide, when the salt was obtained as a voluminous precipitate of green crystals with bronzy lustre. It was purified by crystallisation from warm alcohol, and dried at 100°:

0·2728 gave 26·8 c.c. N_2 at 15° and 768 mm. N = 11·82.

$C_{16}H_{10}O_4N_3K$ requires N = 12·10 per cent.

On heating, this azo-salt decomposed explosively, leaving a voluminous carbonaceous residue.

The sparingly soluble metallic salts of 4-nitro-2-hydroxybenzeneazo-β-naphthol have remarkably intense colours; those of the heavy metals were prepared by mixing an aqueous solution of the metallic salt with an alcoholic solution of the azo-compound and neutralising with dilute ammonia.

Metallic Salts of 4-Nitro-2-hydroxybenzeneazo-β-naphthol.

Metallic ion.	Colour of salt.
1. Alkali and ammonium	Deep blue with green reflex.
Cupric	Dark purple
2. Calcium, Strontium, Barium	Intense purple with green reflex.
Glucinum	Bluish-grey with green reflex.
Magnesium	Intense crimson, slowly deepening.
Zinc	Intense Prussian blue.
Cadmium	Intense bluisb-grey.
Mercuric	Bluish-grey.
3. Yttrium	Intense purple.
Lanthanum	Intense mauve.
Aluminium	Purple-blue, green reflex.
4. Thorium	Bluish-crimson.
Lead	Bluish-green.
5 Chromic	Bluish-grey, green reflex.
Uranyl	Grey-mauve.
7. Manganous	Intense brownish-purple.
8. Nickel	Dark purple.
Cobalt	Dark green.

In one or two instances the difference in colour noticed between pairs of closely-related metals was very striking, as, for example,

the crimson and deep blue lakes obtained with magnesium and zinc respectively. Nickel and cobalt also exhibited noteworthy differences. Cerous and iron salts apparently yielded oxidation products, and not normal lakes. With silver nitrate, reduction took place with formation of an indistinct mirror.

Attempted Preparation of m-*Diazo-oxides from Nitro-derivatives of* m-*Aminophenol.*

4:6-*Dinitro-3-aminophenol.*—Diacetyl-*m*-aminophenol was prepared both by heating *m*-aminophenol for four hours at 150—160° with three to four parts of acetic anhydride and 0·3 part of anhydrous sodium acetate, and by boiling for five minutes a mixture of *m*-aminophenol (1 part), acetic anhydride (5 parts), sodium acetate (0·5 part), and concentrated sulphuric acid (0·02 part). The product was poured into water, the solution partly neutralised with sodium hydrogen carbonate, and the oily diacetyl derivative after solidifying was crystallised from benzene. The yield by the former method was 50—60 and by the latter 85 per cent.

The diacetyl derivative (5 grams) dissolved in acetic anhydride (25 c.c.) was very slowly nitrated with 25 c.c. of nitric acid (D 1·50), cooling the mixture below −5° throughout the operation. The solution, when poured on ice, yielded a yellowish-white pulverulent precipitate of 4:6-dinitrodiacetyl-3-aminophenol (m. p. 157°). This product when hydrolysed by dissolving in concentrated sulphuric acid and warming gently on the water-bath gave rise to 4:6-dinitro-3-aminophenol (m. p. 230°; Meldola and Stephens, T., 1906, **89**, 926; Reverdin and Widmer, *Ber.*, 1913, **46**, 4069).

4-*Nitro-3-aminophenol* and 6-*Nitro-3-aminophenol.*

(i) *m*-Diacetylaminophenol (5 grams) was nitrated by the method described by Meldola and Stephens (*loc. cit.*) and the concentrated acid solution poured on to 100 grams of ice. After thirty minutes the brown, tarry precipitate of 4-nitro-3-acetylaminophenol was collected; the filtrate, made up to 125 c.c., was left overnight, when 6-nitro-3-acetylaminophenol separated as a brown, crystalline mass, a further quantity being obtained by neutralising the filtrate with sodium hydrogen carbonate.

(ii) Nitration of 3-acetylaminophenol led to a sharp separation of the two isomeric nitro-derivatives. *m*-Aminophenol (20 grams) was dissolved in warm acetic anhydride (22 c.c.); on cooling the clear liquid changed into a colourless, crystalline solid consisting of 3-acetylaminophenol. This product, finely powdered, was added slowly to six parts of concentrated nitric acid (D 1·4), cooled by

ice and salt. The mixture, which was stirred thoroughly throughout the nitration to prevent clotting and overheating, was poured on to ice, and the greyish-brown precipitate washed until it became dull grey. This product, amounting to 80 per cent. of the calculated amount, was a mixture of the two nitroacetylamino-*m*-phenols; it was dissolved in hot alcohol, and the solution filtered rapidly. The brownish-purple filtrate deposited almost immediately small, grey crystals of 4-nitro-3-acetylaminophenol, which, after two crystallisations from alcohol, melted at 266°.

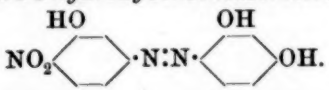
The mother liquor was concentrated to half its original volume, cooled, filtered from a small crop of mixed crystals, boiled with animal charcoal, and concentrated further, when 6-nitro-3-acetylaminophenol separated in brown needles. This product after two crystallisations from alcohol, in which it was very readily soluble, melted at 221°. The foregoing separation of the two isomeric acetyl derivatives was very complete owing to the great difference between their solubilities in alcohol.

The acetyl derivatives were readily hydrolysed by heating on the water-bath with hydrochloric acid (5 per cent. solution); the 6-nitro-compound was decomposed in about half the time required to hydrolyse the 4-nitro-derivative. The resulting 4- and 6-nitro-3-aminophenols separated from the acid solutions on cooling, and were recrystallised from boiling water; they melted respectively at 185° and 157°.

Action of Nitrous Acid on Nitrated m-*Aminophenols.*

The various methods of treatment which had led to the formation of ortho- and para-diazo-oxides from ortho- and para-aminophenols respectively were now applied to the three foregoing nitrated *m*-aminophenols. Diazotisation was effected with sodium nitrite, ethyl nitrite, or nitrous fumes in ethereal, alcoholic, aqueous, or glacial acetic acid solutions, but without obtaining any indication of the formation of meta-diazo-oxides. The diazonium salts, which were first formed, gradually decomposed into tarry, uncrystallisable products with no power of coupling with alkaline resorcinol or β-naphthol. These diazonium salts were characterised by conversion into azo-derivatives, which separated as sparingly soluble alkali salts, and were then set free by mineral acid.

4-Nitro-3-hydroxybenzeneazoresorcinol,



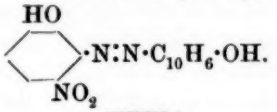
The diazonium chloride from 6-nitro-3-aminophenol did not couple readily with alkaline β-naphthol, although reacting normally

with aqueous or alkaline resorcinol or with β-naphthylamine in aqueous or alcoholic solution. The azo-resorcinol separated from alcohol in dark red crystals melting at 196°, and developing with concentrated sulphuric acid an orange-red coloration permanent after twenty-four hours:

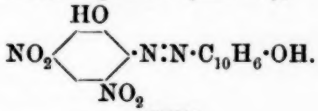
0·0600 gave 7·8 c.c. N_2 at 16° and 750 mm. N = 15·23.

$C_{12}H_9O_5N_3$ requires N = 15·27 per cent.

2-Nitro-5-hydroxybenzeneazo-β-naphthol (XXIV),



(XXIV.)



(XXV.)

This red azo-compound was only sparingly soluble in the ordinary organic media, and did not melt below 260°:

0·1107 gave 12·7 c.c. N_2 at 21° and 748 mm. N = 13·17.

$C_{16}H_{11}O_4N_3$ requires N = 13·59 per cent.

2:4-Dinitro-5-hydroxybenzeneazo-β-naphthol (XXV).

4:6-Dinitro-3-aminophenol dissolved in warm nitric acid (D 1·42) was cooled below 0° and diazotised with ethyl nitrite. The crystals slowly dissolved, and the clear solution after considerable dilution with ice-cold water was added to alkaline β-naphthol. The azo-derivative was crystallised from benzene in brownish-red needles not melting below 260°; it was insoluble in alcohol:

0·0758 gave 9·9 c.c. N_2 at 15° and 750 mm. N = 15·35.

$C_{16}H_{10}O_6N_4$ requires N = 15·82 per cent.

This compound and the preceding azo-β-naphthol developed with concentrated sulphuric acid an intense violet coloration changing slowly to red and then to pink during twenty-four hours.

The authors desire to express their thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
DUBLIN.

[*Received March 24th*, 1915.]

LXVIII.—*The Absorption Spectra of the Vapours and Solutions of Anisole, Phenetole, and Various Derivatives.*

By John Edward Purvis.

In previous communications the author has shown that the physical conditions and the nature and type of the atoms or atomic groups introduced in an oscillatory centre like benzene exercise a powerful influence on the absorption. It was proved, for example, that the vapour bands of the chlorine and bromine derivatives of benzene, and of other substances like phenol and aniline, were not so sharply defined, and were slightly more diffuse than the bands of the simple molecules themselves, and that there was a gradual decrease in the number of bands as the number of such side-chains increased, so that, finally, all the fine bands disappeared, and the absorption was then comparable with the solution phenomena. It was further proved that there was a complete absence of the fine vapour bands in the iodo- and nitro-derivatives of all these substances.

It has been shown (Purvis and McCleland, T., 1912, **101**, 1514) that whereas anisole exhibited a considerable number of vapour bands, the vapour of diphenyl ether had only two diffuse bands which were comparable with the solution bands, and that the vapour bands in *m*-aminophenol were considerably diminished, and in *m*-dimethylaminophenol and azoxybenzene they were completely eliminated, although benzene, aniline, and phenol possessed a large number of such bands (Purvis, T., 1913, **103**, 1088, 1638; 1914, **105**, 590).

The author has continued the investigation with anisole and phenetole and various derivatives of these substances to see how far and in what directions the absorption is influenced by the introduction of different groups in the vibrating nucleus. The substances investigated were: *p*-bromoanisole, phenetole, *p*-fluorophenetole, *p*-bromophenetole, *o*- and *p*-anisidines, *o*- and *p*-phenetidines, *p*-azoxyanisole, and *p*-azoxyphenetole.

The experimental conditions have been described before.

Anisole and p-*Bromoanisole.*—The vapour bands and the solution bands of anisole have already been described (*loc. cit.*). It was shown that the number of narrow vapour bands was forty-one, whereas there were only two rather wide and diffuse solution bands; but when the vapour was subjected to higher temperatures and pressures the bands became wider and more diffuse, and finally attained the appearance of the solution phenomena. The two solution bands may be considered to correspond with two groups of

well-marked vapour bands, and the following numbers give the positions of the heads of these bands. It was not possible to measure the edges of the diffuse solution bands, and therefore the middle of the strongest part, which was towards the more refrangible edge, was measured, and the strongest constituent of the vapour bands on its more refrangible edge was also measured:

Solution bands of anisole.	Vapour bands of anisole.
λ	λ
2800	2749, a group of 10 bands, fairly strong.
2725	2681, a group of 8 bands, fairly strong.

The more refrangible vapour bands between λ 2680 and λ 2516 do not appear in the solutions; but the rapid absorption to λ 2560 probably represents these bands weakened and widened by the solvent. It may be mentioned that the vapour bands of anisole are like those of phenol (*loc. cit.*), except that several of the weaker, more refrangible bands of the former are absent.

In *p*-bromoanisole, solutions varying from $M/100$, $M/1000$, and $M/10{,}000$ were examined, and at thicknesses from 2 mm. to 30 mm. The absorption was not unlike that of the corresponding solutions of anisole, but the two bands were much weaker and wider and more diffuse than the corresponding bands of the latter.

The vapour of *p*-bromoanisole was examined at temperatures and pressures varying from 16° and 770 mm. to 90° and 930 mm., and eight bands were observed between λ 2898 and λ 2700. These bands were wider and more diffuse than the corresponding bands of anisole, even at the lowest temperatures and pressures, and were shifted more towards the red end. The narrower bands of anisole had not only decreased in number, but were very diffuse; they were also more diffuse and fewer than the vapour bands of *p*-bromophenol (*loc. cit.*). The position of the corresponding solution and vapour bands are:

Solution bands of *p*-bromoanisole.	Vapour bands of *p*-bromoanisole.
λ	λ
2910	2869, a strong wide band ranging to λ 2880, which showed doubtful signs of division.
2820	2790, a moderately strong band ranging to λ 2778, which also showed doubtful signs of division.

Phenetole, p-*Fluorophenetole*, and p-*Bromophentole*.—The absorption phenomena of the phenetole solutions were very like those of anisole. There were two well-marked bands (Fig. 1, I, upper curves), and these gradually widened into each other to produce

one large band at greater thicknesses, with a rapid extension of the absorption on the more refrangible side.

The vapour of phenetole was examined at temperatures ranging from 16° and 757 mm. to 90° and 917 mm., and forty bands were observed which were measured and classified. The bands were very like those of anisole (*loc. cit.*), except that they were shifted slightly more towards the red, and they were a shade more diffuse. Two of the stronger groups of the vapour bands correspond with the two solution bands, and the following numbers give the heads of these bands, together with two corresponding groups of anisole vapour bands:

Solution bands of phenetole.	Vapour bands of phenetole.	Vapour bands of anisole
λ	λ	λ
2800	2750, a strong group of 8 bands.	2749, a strong group of 9 bands.
2720	2682, a strong group of 9 bands.	2681, a strong group of 8 bands.

There were other much weaker bands beyond λ 2682, which would probably correspond with the rapid absorption in the solution between 1/λ 3715 and 1/λ 4080.

In *p*-fluorophenetole the solution phenomena were not unlike those of phenetole, except that the bands were not so well defined. The two bands were weaker and more diffuse; but, like the others, they widened into each other, and formed one large band at greater thicknesses.

The vapour of *p*-fluorophenetole was examined at temperatures ranging from 10° and 763 mm. to 90° and 923 mm., and thirty-one bands were observed between λ 2860 and λ 2684. These bands were clear and well defined, and were fewer in number than in phenetole; the bands on the more refrangible side of the latter were eliminated in *p*-fluorophenetole. The bands were measured and classified. There are several well-defined groups amongst them, two of which can be compared with the two solution bands:

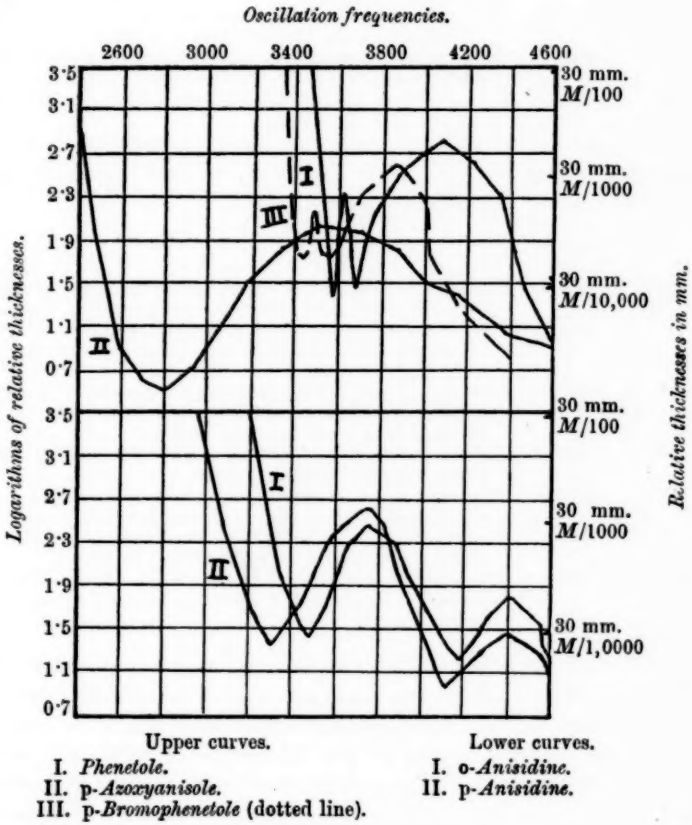
Solution bands of *p*-fluorophenetole.	Vapour bands of *p*-fluorophenetole.
λ	λ
2900	2852, a group of 5 bands moderately strong.
2830	2780, a group of 5 bands, fairly strong.

In *p*-bromophenetole the solutions showed two bands not unlike those of phenetole itself, but they were much weaker and wider and more diffuse (Fig 1, III, upper curves). The vapour of *p*-bromophenetole exhibited eight bands between λ 2924 and λ 2792 at temperatures and pressures ranging from 16° and 750 mm. to 100° and 926 mm. As compared with the vapour bands of *p*-bromoanisole, the bands were more diffuse and weaker; and, as compared

with the vapour bands of phenetole and *p*-fluorophenetole, they were wider and more diffuse and fewer in number. Two of the stronger groups of the vapour bands are comparable with the two weak diffuse solution bands:

Solution bands of *p*-bromophenetole.	Vapour bands of *p*-bromophenetole.
λ	λ
2910	2894—2861, a strong band, stronger on the more refrangible edge, which shows doubtful signs of division.
2810	2802—2791, a very weak diffuse band.

FIG. 1.



Upper curves.

I. *Phenetole.*
II. p-*Azoxyanisole.*
III. p-*Bromophenetole* (dotted line).

Lower curves.

I. o-*Anisidine.*
II. p-*Anisidine.*

o- *and* p-*Anisidines.*—The solution curves of these substances have been drawn (Fig. 1, I and II, lower curves). It will be noticed that both show two well-defined bands, and that those of the para-compound are shifted considerably more towards the red.

The vapour of *o*-anisidine was examined at temperatures and pressures varying from 13° and 760 mm. to 100° and 936 mm., and the following phenomena were observed:

$t°$.	Pressure in mm.	
50	840	The rays were feebly absorbed between λ 2920 and λ 2780, and then transmitted to λ 2410; they were then completely absorbed to the Cd line λ 2329; and from here the series of Cd lines to λ 2144 were fairly well marked.
55	850	The rays were fairly well absorbed between λ 2940 and λ 2780; then transmitted to about λ 2420: also the Cd lines 2265, 2194, 2144 were fairly well marked.
65	870	The rays were almost completely absorbed between λ 2970 and λ 2750, and then transmitted to λ 2450.
75	890	The rays were completely absorbed between λ 2990 and λ 2710, and then transmitted to λ 2480.
85	910	The rays were completely absorbed from λ 3010, except that the Cd line 2573 was fairly well marked.
95	920	The rays were completely absorbed from about λ 3020

The vapour of *p*-anisidine was examined at temperatures and pressures varying from 14° and 760 mm. to 100° and 936 mm., and the following phenomena were observed:

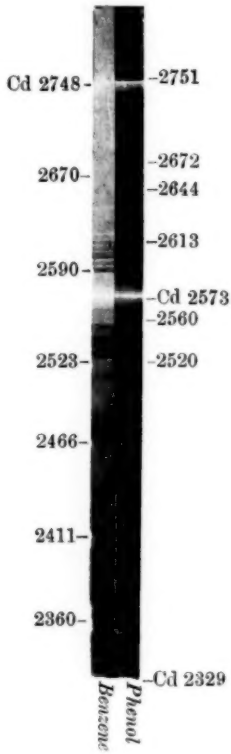
$t°$.	Pressure in mm.	
65	870	The rays were transmitted to Cd 2144, but they showed signs of weakening between λ 2400 and λ 2340.
70	880	The rays were transmitted to λ 2440, and then absorbed to Cd 2329; from here the Cd lines 2329 to 2144 were quite strong.
75	890	The rays were feebly absorbed between λ 3100 and λ 2960, and then transmitted to λ 2450; the Cd lines 2329 to 2265 were fairly well marked.
80	900	The rays were fairly well absorbed between λ 3130 and λ 2900, and then transmitted to λ 2480.
85	910	The rays were almost completely absorbed between λ 3140 and λ 2850, and then transmitted to λ 2510.
95	920	The rays were completely absorbed between λ 3150 and λ 2780, and then transmitted to λ 2580.
100	936	The rays were absorbed from λ 3200, except that between λ 2700 and λ 2580, there was a very weak transmission.

o- *and* p-*Phenetidines.*—The alcoholic solutions and the vapours of these two substances were also examined under similar conditions of temperature and pressure, and similar phenomena were observed, except that the two bands of the heavier molecules were shifted more towards the red. The results are therefore not described in detail. It is, therefore, clear from the observations that neither the anisidines nor the phenetidines exhibited any of the numerous vapour bands shown by aniline or phenol (*loc. cit.*), and that the few bands found in the halogen derivatives of anisole and phenetole have also completely disappeared.

p-*Azoxyanisole and* p-*Azoxyphenetole.*—Solutions of these two

FIG. 2.

The absorption spectra of the vapours of phenol and benzene.



The wave-lengths of the heads of the chief series of bands of benzene vapour are marked below, and the wave-lengths of phenol above, the photograph. The series of sharply-defined bands of phenol between 2644 and 2520 are well marked.

[*To face p.* 665].

substances showed similar absorption to that of azoxybenzene (*loc. cit.*). The absorption curve of *p*-azoxyanisole has been drawn (Fig. 1, II, upper curves) to show the great differences between its type of absorption and that of several of the other substances. The positions of the heads of the solution bands of the azoxy-compounds compared with azoxybenzene are:

	λ
Azoxybenzene	3225
p-Azoxyanisole	3550
p-Azoxyphenetole	3600

The vapours of the two substances were not examined because of their comparatively high melting points; but, as in azoxybenzene which has been examined (*loc. cit.*), it is scarcely likely that the vapours would exhibit any narrow bands. The great shift of the solution bands of *p*-azoxyanisole and *p*-azoxyphenetole as compared with azoxybenzene is worthy of note, because a similar great shift takes place in the vapour and solution bands of phenol as compared with benzene.

Witte ("Zur Struktur der ultravioletten absorptionspektren des Benzols und seiner monoderivate," *Diss.*, Leipzig, 1914) demurs to the statement (Purvis and McCleland, T., 1913, **103**, 1088) that the absorption spectrum of phenol does not show any resemblance to that of benzene described by Hartley (*Phil. Trans.*, 1907, [*A*], **208**, 475). At the time of the observations the photographs of phenol were compared with the reproductions of the photographs of benzene as published in Hartley's memoir. In order to test this further, the author has photographed the spectra of approximately equal quantities of benzene and phenol in a 200 mm. tube. The photographs were originally enlarged to twice the size, and even in the smaller reproductions (Fig. 2) it will be noticed that there is a striking difference between the two spectra. The phenol bands are shifted very considerably towards the red as compared with those of benzene, and the heads of the various groups are clear and well defined. When the plates are arranged so that the heads of the strongest bands of both substances lie just below one another, there does not appear to be any close resemblance between the various groups of bands, except that some groups in both are stronger than others.

General Results.

The outstanding results of the observations are:

(1) The smaller number of vapour bands of *p*-bromoanisole, and their more diffuse appearance, as compared with the vapour bands of anisole.

(2) The considerable number of vapour bands of phenetole,

which are comparable with those of anisole; the decreased number of vapour bands of *p*-fluorophenetole, and still more of *p*-bromophenetole; and the more diffuse appearance of the bands of the latter compound.

(3) The absence of the numerous vapour bands when the substances are in solution, and the more diffuse appearance of the solution bands of *p*-bromoanisole, *p*-fluorophenetole, and *p*-bromophenetole as compared with the solution bands of anisole and phenetole.

(4) The complete absence of any narrow vapour bands in the anisidines and phenetidines, and the close similarity of their solution and vapour bands.

(5) The similarity of the large solution bands of *p*-azoxyanisole and *p*-azoxyphenetole with that of azoxybenzene.

(6) The substitution in all the substances at higher temperatures and pressures of all the fine vapour bands by wide and diffuse bands which are comparable with the solution bands.

The introduction of an aliphatic group in phenol, as in anisole and phenetole, does not alter fundamentally the type of absorption in phenol itself, although the bands are not so sharp; but when fluorine or bromine is introduced in the nucleus there is a considerable decrease in the number of the finer bands, and they are much wider and more diffuse, particularly in the bromine compounds. Such changes may be caused by the introduced atoms or atomic groups damping and neutralising the fundamental electronic oscillations of the nucleus, whereby the period and amplitude are considerably altered; when the amino-group is introduced, as in the anisidines and phenetidines, the complex oscillations are completely neutralised, and a single large absorption band takes the place of the numerous bands found in aniline and phenol.

The comparatively wide and diffuse solution bands may indicate that the solvent produces an association of the molecules whereby the oscillations are partly mutually neutralised and partly exercised against this constraining force. Such a close association may also be produced when the molecules of the vapour are forced closer together by the constraining influence of increased pressures, for, as the author has also shown in previous communications, the absorption bands of the vapours are, under such conditions, similar to those of the solutions, and also to those of very thin films where the molecules are definitely in closer association. This intimate connexion of the vibrating centres is more obvious when there are two benzene radicles in the molecule, as in the azoxy-compounds, or as in diphenyl (Purvis, T., 1914, **105**, 590), and the result is apparent in a simpler type of absorption band than that found in

anisole or phenetole or benzene. Moreover, the incomplete neutralisation of the valencies of the nitrogen atoms, which act as oscillatory centres, is another powerful influence, particularly in the production of the colour of the azoxy-compounds.

I desire to thank the Chemical Society for a grant in aid of the expenses of this investigation.

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CAMBRIDGE. [*Received, April 8th,* 1915.]

LXIX.—*The Relation between Viscosity and Chemical Constitution. Part IX. The Viscosity and Fluidity of the Aliphatic Acids.*

By ALBERT ERNEST DUNSTAN.

IN two recent papers (T., 1913, **103**, 127; 1914, **105**, 782) it has been shown that the curves connecting the logarithms of viscosity with molecular weights in an homologous series are linear. In the case of those members of high molecular weight, however, this statement should be modified, since, in all such cases, there appears to be a falling off in the value of the viscosity.

The homologous series of the fatty acids present several marked peculiarities. Firstly, the viscosities of formic and acetic acids are much higher relatively than those of the succeeding members; in fact, formic acid is more viscous than acetic acid, so that the initial homologous increment has a negative value. Secondly, the average value of the homologous increment throughout the series is far in excess of that which obtains in such series as the esters, ethers, paraffins, and ketones, where a very fair agreement is obtained between the various CH_2 differences. It was therefore thought desirable to make a closer study of the viscosities of the fatty acids, particularly as the only other determinations on record are those of Gartenmeister at 20° and of Thorpe and Rodger for the first four members.

EXPERIMENTAL.

The acids used were the purest specimens obtainable. The first four members gave results which were in good agreement with those obtained by Thorpe and Rodger, with the exception of butyric acid, which showed a slightly higher value at 25°. One

litre of this acid was therefore carefully fractionated, but still the value was high, agreeing, as a matter of fact, with Gartenmeister's number (0·0146, as against 0·0142 of Thorpe and Rodger). Precisely similar lack of agreement was found with an acid which was prepared by the malonic synthesis. At higher temperatures the discrepancy disappears, and at 70° the two curves are coincident.

In the case of the acids which were liquid at the ordinary temperature, phosphoric oxide was used as a desiccating agent. The solid acids were crystallised repeatedly from absolute alcohol and light petroleum.

Every fraction made use of was examined refractometrically in connexion with another investigation which Mr. F. W. Linch is making in this laboratory. Unfortunately, however, refractometric analysis cannot indicate whether the natural products are contaminated with traces of *iso*-derivatives.

The valeric acid was also prepared from malonic ester, and agreed satisfactorily with the natural acid.

Refractometric evidence showed that the specimens of octoic and decoic acids were impure, and it was not found possible to obtain the pure acids.

Pure specimens of pelargonic, myristic, palmitic, and stearic acids were kindly lent by Dr. Le Sueur, and afforded values in close agreement with those of materials which had been already used.

Densities were determined in a 2 c.c. Sprengel pyknometer and in a 5 c.c. gravity bottle, and were plotted along with the values given by Beilstein. In the majority of cases a linear curve could be constructed, from which the value required at any particular temperature could be obtained by interpolation.

The following new values may be given, in all cases in reference to water at 4°:

Valeric acid	$0{\cdot}9387_{20°}$	$0{\cdot}9205_{40°}$	$0{\cdot}9104_{50°}$	$0{\cdot}8924_{70°}$
Hexoic acid	$0{\cdot}9234_{25°}$	$0{\cdot}9276_{30°}$	$0{\cdot}9108_{40°}$	$0{\cdot}873_{90°}$
Heptoic acid	$0{\cdot}9172_{20°}$	$0{\cdot}9011_{40°}$	$0{\cdot}8909_{50°}$	$0{\cdot}876_{70°}$
Nonoic acid	$0{\cdot}9057_{20°}$	$0{\cdot}9022_{23°}$	$0{\cdot}8901_{40°}$	$0{\cdot}883_{50°}$
Lauric acid	$0{\cdot}8690_{50°}$	$0{\cdot}8544_{70°}$	$0{\cdot}8386_{90°}$	—
Myristic acid	$0{\cdot}8528_{70°}$	$0{\cdot}8394_{90°}$	—	—
Palmitic acid	$0{\cdot}8487_{70°}$	$0{\cdot}8347_{90°}$	—	—
Stearic acid	$0{\cdot}849_{70°}$	$0{\cdot}835_{90°}$	—	—

Viscosity.—Every acid was examined in at least two viscometers, and very close agreement was obtained. The viscometers were calibrated in accordance with the method given by Thole (T., 1914, **105**, 2010).

Thus for viscometer β the following numbers were obtained:

Calibrating liquid.	Time of flow in seconds.	log. constant.
Chloroform	75	$\bar{5}$·683
Acetone	80	$\bar{5}$·688
Benzene	140	$\bar{5}$·693
Toluene	130	$\bar{5}$·693
Ethylene dibromide	148	$\bar{5}$·694
Ethyl alcohol	274	$\bar{5}$·701
n-Propyl alcohol	480	$\bar{5}$·710
*iso*Butyl alcohol	800	$\bar{5}$·711

A smooth curve was drawn through these values for the log. constant, and hence the appropriate constant for any particular time of flow was obtained by interpolation. In the previous paper, to which reference has been made, the viscometers were calibrated with the same liquid at different temperatures, with the result that the long times of flow for the higher acids required a higher value of the log. constant, and consequently the values given are too low. When, however, the viscosities are recalculated, using constants determined by this new method, satisfactory agreement is reached. Thus for two cases:

		Old value.	New value.
70°	Valeric acid	0·00993	0·00994
70°	Palmitic acid	0·0890	0·0892

Results.

Propionic Acid.

$t°$.	$\eta \times 10^5$.	$\log \eta . 10^5$.	ϕ.
20	1099	3·0414	90·9
30	956	2·9805	104·6
40	841	2·9248	118·9
60	668	2·8248	149·7
80	544	2·7256	188·1
90	495	2·6946	202·0

Butyric Acid.

20	1538	3·1869	65·03
30	1301	3·1142	76·9
50	971	2·9875	102·9
70	756	2·8785	132·3
90	6045	2·7813	165·4

Valeric Acid.

16·5	2415	3·3829	41·41
20	230	3·3617	43·48
25'	205	3·3119	48·76
50	1315	3·1189	76·05
70	986	2·9939	101·4
90	753	2·8768	132·8

Hexoic Acid.

$t°$.	$\eta \times 10^5$.	$\log \eta . 10^5$.	ϕ.
16·1	3560	3·5518	28·06
20	3230	3·5087	30·99
25	2840	3·4538	35·18
40	2120	3·3267	47·13
50	1750	3·2433	57·11
70	1290	3·1118	77·31
90	981·0	2·9918	101·9

Heptoic Acid.

17·5	4600	3·6630	21·73
20	4330	3·6365	23·10
25	3800	3·5800	26·30
50	2300	3·3617	43·48
70	1610	3·2068	62·12
90	1190	3·0755	84·05

Nonoic Acid.

20	8080	3·9074	12·38
25	7000	3·8451	14·29
50	3790	3·5786	26·38
70	2410	3·3820	41·50
90	1730	3·2386	57·73

Lauric Acid.

50	7300	3·8633	13·70
60	5610	3·7489	17·82
70	4430	3·6465	22·57
80	3620	3·5583	27·65
90	2990	3·4758	33·44

Myristic Acid.

60	7430	3·8708	13·47
70	5835	3·7660	17·14
80	4645	3·6670	21·53
90	3810	3·5810	26·24

Palmitic Acid.

70	7835	3·8942	12·76
80	6130	3·7877	16·30
90	500	3·6989	20·00
95	447	3·6504	22·37

Stearic Acid.

70	9870	3·9945	10·13
80	7720	3·8876	12·95
90	6098	3·7852	16·40
95	5473	3·7382	18·27
98	518	3·7140	19·32

Discussion of Results.

The values for each acid fall on a smooth curve, which shows the rapid decrease in the viscosity as the temperature rises.

The logarithms of viscosities plotted against molecular weights give for each temperature an apparently linear curve between the limits C_3–C_9. Below this limit there is seen the abnormally high values of the first two members, and above it there occurs a steady diminution in the homologous increment. Although the main part of the curve appears to be linear, a close inspection of the CH_2 differences shows some irregularity between C_5 and C_6.

Log. CH_2 differences at 50°.

Number of carbon atoms.	Δ log. CH_2.
3	0·1407
4	0·1596
5	0·1419
6	0·1262
7	—
9	0·1325

Log. CH_2 differences at 50°.

Number of carbon atoms.	Δ log. CH_2.
3	0·1100
4	0·1315
5	0·1244
6	0·1184
7	0·1130
9	0·0919
12	—

Log. CH_2 differences at 70°.

Number of carbon atoms.	Δ log. CH_2.
3	0·0992
4	0·1154
5	0·1169
6	0·0950
7	0 0876
9	0·0882
12	0·0597
14	0·0640
16	0·050
18	—

Log. CH_2 differences at 90°.

Number of carbon atoms.	Δ log. CH_2.
3	0·0867
4	0·0952
5	0·1143
6	0·0837
7	0 0815
9	0·0791
12	0·0526
14	0·0589
16	0·0431
18	—

It thus appears that in the case of the acids, at any rate, the additivity of log. viscosity is very considerably affected by constitutive influences, which, of course, to a greater or less extent affect every additive property.

In recent years the work of Bingham (T., 1913, **103**, 959) has led to the opinion that fluidity, and not viscosity or log. viscosity, is really the additive property. This opinion has been vigorously attacked, amongst others by Kendall (*Meddelanden K. Vetensk. Nobelinstitut*, 1913, **2**, No. 25). It thus appeared of some interest to calculate the fluidities of the fatty acids at various temperatures, and to see to what extent this held good. Bingham asserts, for example, that at the value $\phi = 300$, additive atomic and group values for absolute temperature are obtained, which synthesise into molecular values agreeing well enough with the known values.

An example will make this clear.

Butyric Acid, $C_3H_7 \cdot CO_2\phi H$.

Temperature values at $\phi = 300$:

4C	$= 4\times$	$-110{\cdot}2°$	$= -440{\cdot}8°$
8H	$= 8\times$	$67{\cdot}8°$	$= +542{\cdot}4°$
2O	$= 2\times$	$27{\cdot}1°$	$= +\ 54{\cdot}2°$
Double bond in carbonyl group	$=$	$-131{\cdot}3°$	$= -131{\cdot}3°$
			$287{\cdot}1°$

In actual fact the temperature at $\phi = 300$ is 426·5°. The discrepancy is ascribed by Bingham to association, and consequently he calculates the association factor to be $426{\cdot}5/287{\cdot}1 = 1{\cdot}48$.

In the opinion of the author neither log. viscosity nor fluidity is rigidly additive (nor is any other physical property except mass). When, however, one considers that fluidity is the differential-coefficient of log. viscosity, it is not surprising, when one examines the fluidity curves, to find that they are decidedly similar to the log. viscosity curves. Neither is absolutely linear, but both approximate to linearity to a greater extent than the viscosity curves.

The author's thanks are due to the Government Grant Committee of the Royal Society for a grant in aid of this work.

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LXX.—*A Method for Distinguishing Tautomeric, Isomeric, and Polymeric from Polymorphic Substances.*

By NEVIL VINCENT SIDGWICK.

THERE are many examples of substances occurring in two mutually convertible modifications, where it is uncertain whether the difference is due to a difference in the structure of the molecules (tautomerism, dynamic isomerism, polymerism), or in the arrangement of identical molecules in the crystals (physical dimorphism, polymorphism).

The essential distinction between the two phenomena is this. If the forms are polymorphic, the differences between them will be confined to the solid state, and will disappear in solution; they will be manifested only in the properties of the solid modifications, either alone (crystalline form, refractive index, density, etc.), or in

contact with a liquid or gaseous phase (melting point, solubility, vapour pressure). The solutions or vapours which the two forms give will be identical. On the other hand, if the modifications are tautomeric (or dynamically isomeric or polymeric) the difference will persist in the liquid state also, at any rate for a time.

The general methods used for determining to which of these two categories a particular compound belongs, depend on this distinction. They all aim at ascertaining whether the solutions given by the two forms are identical or not. This, however, is often a difficult matter, especially in view of the danger that tautomeric equilibrium may become established in the solution during the experiment, which would cause the two solutions, although initially different, to appear to be the same.

One method which has been largely used consists in dissolving each form separately in a solvent, and seeing whether it crystallises out unchanged on cooling, or whether the same form separates from both solutions; it is assumed that in the former case the solutions are different and the substances tautomeric, and that in the latter they are polymorphic. Unfortunately, this test is liable to fail on both sides. The forms may be tautomeric and the solutions originally different, and yet tautomeric equilibrium may be established during the experiment (especially under the influence of the necessary rise of temperature), and each solution may yield the same (stable) form; whilst on the other hand, where each form separates unchanged from its own solution, this may be due not to any difference in the two solutions, but to infection, that is, to the presence in each of undissolved nuclei of the form used to make it up.

In the face of these difficulties, the following method is suggested for determining whether the difference of the two forms persists in solution or not.

Let *A* be the more soluble of the two forms *A* and *B*. A saturated solution of *A* is made in a suitable solvent, and to this (at constant temperature) is added some solid *B*. If the forms are polymorphic, and both give the same molecules in solution, then since the solution is saturated with *A*, which is the more soluble form, *B* will not dissolve; on the contrary, since *B* is less soluble, some of the solute will crystallise on it, and the solution will become more dilute, although this change may be too small to be detected. At any rate, the concentration of the solution will not increase. If, however, the forms are tautomeric, then *A* and *B* will each dissolve as such, and when *B* is added to the solution of *A*, it will dissolve irrespective of the presence of *A* (provided that the tautomeric change is not too rapid), and the solution will

become stronger. Thus we know that if the concentration of the solution increases when *B* is added, the forms are tautomeric; if they are polymorphic it will not increase, and may diminish.

The simplest way of discovering what change, if any, occurs in the concentration of the solution on adding the second form, is to measure its freezing point. This has the further advantage that the use of a low temperature diminishes the danger of tautomeric change. The experiment can be carried out in the usual Beckmann apparatus. The freezing point of the solvent having been determined, some of the substance, finely powdered, is added, and the solution, having been warmed a few degrees above its freezing point, is vigorously stirred, and its freezing point observed. This process is repeated, with the addition of more of the substance each time, until the freezing point, which at first falls steadily, becomes constant. Three or four repetitions are usually sufficient. The second form is then added in the same way, and the freezing point again determined. If there is any change, a further quantity is added, and the process repeated until a constant reading is obtained. If the solubilities of the two forms are already roughly known, and if it is also known which is the more soluble, no further measurements are required. Should there be any doubt about this, the depression caused by the second form alone should also be observed.

From the magnitude of the depression produced by each form alone, it is possible to calculate the approximate solubility of the form in benzene at the freezing point (that is, at about 5°), on the assumption that the substance is not associated.

It is obvious that isomeric and polymeric substances will give the same results as tautomeric; what the test really determines is whether the molecules in the solution derived from the two forms are the same or different. On the other hand, tautomeric substances with a very high velocity of change will appear to be polymorphic, since the solute will have attained tautomeric equilibrium before the measurements can be made.

Experimental.

The solvent employed in all the following experiments was benzene, although obviously any other solvent the melting point of which is not too high or too low could be used. The benzene was distilled over sodium before use. As benzene is known to absorb readily small quantities of moisture, an attempt was made to discover whether this would introduce any perceptible error. A specimen of benzene was examined immediately after distillation over sodium, and was compared with others which had been treated

in the same way, in one case two months, and in the other two years before, and had been kept in the meantime without any special precautions to exclude moisture. The differences in freezing point did not exceed 0·01°. In order to determine the maximum effect of moisture, the freezing point of recently distilled benzene was measured, and then about 0·5 c.c. of water added to it in the apparatus; on vigorous stirring the water only partly dissolved. The depression in the freezing point so produced was 0·042°. It does not, therefore, appear that the water absorbed during an experiment is likely to cause any serious error. The water already present in the benzene used (if any) will depress the freezing point of the solvent itself and that of the solution to the same extent (unless it reacts with the solute), and hence its effect will be eliminated from the final result.

The depression of 0·042° obtained for a saturated solution of water in benzene corresponds, if we assume the molecular weight of the water to be 36, with a solubility of 0·31 gram per litre at 5°. According to Herz (*Ber.*, 1898, **31**, 2671) a litre of benzene at 22° dissolves 2·11 c.c. of water. In spite of the difference of temperature (the vapour pressure of water is about three times as great at 22° as at 5°), this value is much higher than one would expect from the cryoscopic measurements. It is possible that the association factor of water in benzene is more than 2; but the method used by Herz seems likely to give too high results.

(1) *Phthalylphenylhydrazide*, $C_6H_4<^{CO}_{CO}>N\cdot NH\cdot C_6H_5$.—The materials, and also the methyl derivative (2) below, were kindly lent me by Dr. Chattaway and Mr. W. J. Lambert, who have been investigating the stability of the forms in detail, and will shortly publish their results. The substance occurs in three forms: *A*, bright yellow (m. p. 184°); *B*, pale yellow (m. p. 184°); *C*, white (m. p. 216°):

Depression of f. p. by	*A*	= 0·114°.	Solubility 5·5 grams per litre.
,, ,,	*A*+*B*	= 0·116°.	
,, ,,	*A*+*B*+*C*	= 0·142°.	
,, ,,	*C* alone	= 0·022°.	Solubility 1·1 grams per litre.

Hence *A* and *B* are polymorphic, whilst *C* is isomeric or tautomeric with them. The smallness of the increase in depression (0·026°) caused by adding *C* to the solution saturated with *A* and *B* made it necessary to measure the depression produced by *C* alone.

(2) *Phthalylphenylmethylhydrazide*,

$$C_6H_4<^{CO}_{CO}>N\cdot N(CH_3)\cdot C_6H_5.$$

—*A*, yellow, unstable (m. p. 127°); *B*, white, stable (m. p. 127°). This

is a much more soluble substance, and the difference in the solubility of the two forms is quite perceptible by this method. The *A* form gave a depression of 2·428° (124 grams per litre); on adding the *B*, the depression diminished at once to 2·372°, and in the course of a few hours to 2·086°, where it remained stationary. The forms are therefore polymorphic. The difference in depression is 15 per cent. Mr. Lambert's results, by the direct determination of the solubility, indicate a difference in solubility of about 30 per cent. at this temperature.

(3) p-*Bromoacetanilide*.—This and the next substance were given me by Dr. Chattaway. *A* form, needles, unstable (m. p. 168°); *B*, short prisms, stable (m. p. 168°):

Depression with *A*	0·048°.	Solubility 2·4 grams per litre.
„ *A*+*B*.....	0·049°.	

The two forms are polymorphic.

(4) 2:4 *Dibromoacetanilide*.—*A*, needles, unstable (m. p. 146°); *B*, prisms, stable (m. p. 146°):

Depression with *A*	0·383°.	Solubility 11·5 grams per litre.
„ *A*+*B*	0·352°.	

Here, as in (2), the difference in solubility is quite perceptible, and the two forms are polymorphic.

(5) p-*Nitrophenol*.—This is well known to occur in two forms (Barker, P., 1911, **27**, 158): *A*, pale yellow, not affected by light; *B*, pale yellow, turning red in light. The substance was completely freed from traces of the ortho-compound by distillation in a current of steam, and purified by repeated crystallisation from water at the ordinary temperature. This gives form *A*. *B* was prepared from this by transformation in the presence of water at 25°. The change required nearly two months, in spite of the fact that the solubility in water is about 10 per cent. at this temperature. At 35° the change takes nearly a week, and at 55° (in the presence of toluene) several hours. The *B* (reddening) form is therefore stable between 25° and 55°. The depression of freezing point was, however, found to be greater with *B* than *A* (0·25, as against 0·22°). Unless this is due to an impurity, *A* must be the stable form at 5°, and there must be a transition point between 5° and 25°. Experiments have been begun to test this point by seeing whether *B* changes into *A* in the presence of water when kept in ice; but the change is so slow that they cannot be complete for some time.

The slowness of the change, and the fact that one form alone is affected by light, suggest that the difference is chemical, and that

the substances are tautomeric. The cryoscopic results contradict this view, and indicate that the two forms are polymorphic:

Depression with *A* alone	0·224°.	
„ *B* alone	0·249°.	Solubility 7·1 grams per litre.
„ *A*+*B*	0·243°.	

(6) *Benzoylcamphor* (enol and ketone).—This substance is a familiar example of dynamic isomerism. Its behaviour was originally described by Forster (T., 1901, **79**, 987; 1902, **81**, 160; 1903, **83**, 98), and subsequently examined in detail by Dimroth and Mason (*Annalen*, 1913, **399**, 91). I am indebted to Dr. Mason for the specimens used. It is so excessively soluble in benzene that a special form of apparatus had to be used, and the results are only approximate. But they are sufficient to confirm the method, and to show that the two forms are tautomeric:

Depression with enol alone	4·9°.	Solubility 256 grams per litre.
„ enol+ketone	7·0°.	

(7) *Phthalylhydroxylamine*, $C_6H_4<\begin{matrix}CO\text{———}\\C(:NOH)\end{matrix}>O$.—Lent me by Dr. Chattaway; it occurs in two forms (Lassar-Cohn, *Annalen*, 1880, **205**, 295; Orndorff and Pratt, *Amer. Chem. J.*, 1912, **47**, 93): *A*, white (m. p. 220—226°); *B*, yellow (m. p. 220—226°):

Depression with *A* alone	0·010°.	Solubility 0·33 gram per litre.
„ *A*+*B*	0·020°.	

Presumably the two forms are tautomeric. The depression is so small that no great value attaches to the result. It is, however, confirmed by the observation that a cold saturated solution of *A* in alcohol is colourless, and one of *B* yellow. On boiling, the solution of *B* becomes paler, and that of *A* yellow, the two having to the eye the same colour.

(8) *Camphoric Anhydride*.—This substance was examined in order to show that any chemical difference in the two forms, even that of optical antimerism, is sufficient to cause the substance to respond to the test:

Depression with dextro-form alone	0·991°.	Solubility 37·5 grams per litre.
„ dextro- +lævo-forms	1·787.	

The two are therefore isomeric. The forms must be equally soluble. The depression observed with the two together is 10 per cent. less than twice that given by the dextro-form alone. This may be due to the diminution of the solubility of each owing to the presence of the other (the stronger solution contains 7 per cent. of anhydride). It is to be noticed that any formation of a racemate in solution, provided that this did not crystallise out, would lead to a corresponding increase in the depression; indeed, this method

might be used to detect the presence of racemic compounds in solution.

(9) *Phenylglyoxalphenylhydrazone*, $C_6H_5{\cdot}CO{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$.—Prepared by the method described by Bamberger and Schmidt (*Ber.*, 1901, **34**, 2009). It occurs in two forms: *A*, m. p. 114—117°, more soluble (from light petroleum); *B*, m. p. 136—140°, less soluble (from alcohol). The account which they give of the stability relations of the two forms is very perplexing, and the substance has been quoted by Dimroth (*Annalen*, 1910, **377**, 137) as a case where the stability of the form is determined by the solvent in contact with it. I am engaged in examining the behaviour of the substance in detail. The cryoscopic test is quite definitely in favour of tautomerism; there is an obvious possibility of *cis-trans*-isomerism:

Depression with *A* alone	2·105°.	Solubility 52·6 grams per litre.	
„ *B* alone	0·116°.	„ 2·9	„ „
„ *A*+*B*	2·200°.		

(10) *Methylcryptopines*, $C_{22}H_{25}O_5N$.—Prof. W. H. Perkin has recently obtained by the methylation of cryptopine three substances of the above composition: *A*, m. p. 150°; *B*, m. p. 128°; *C*, m. p. 110°, and has given me specimens of them to examine. The substances crystallise with extreme sluggishness, rendering it difficult to secure saturation at the freezing point:

Depression with *A* alone	0·136°.	Solubility 10 grams per litre.	
„ *B* „	0·381°.	„ 30	„
„ *C* „	1·452°.	„ 110	„

When *A* was added to the saturated solution of *B*, the depression began to diminish at once; in an hour it was 0·362°, and five hours later it was 0·339°. This shows that *A* and *B* are polymorphic. When *A* was added to the saturated solution of *C*, the depression slowly increased to 1·540°, that is, by 0·088°, the depression produced by *A* alone being 0·136°. Hence *A* and *C* are isomeric or tautomeric. Thus it appears that *A* and *B* are polymorphic forms of the same substance, whilst *C* has a different structure.

I wish to express my thanks to those gentlemen who have lent me substances for use in this work. I should be very glad if anyone who has observed examples of polymorphic or tautomeric substances would send me specimens to examine. The quantity needed for the test is usually from 1 to 10 grams, according to the solubility; the mixture of the forms can be recovered without sensible loss.

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[*Received, March 26th*, 1915.]

LXXI.—*The Rate of Hydration of Camphoric Anhydride.*

By Bernard Howell Wilsdon and Nevil Vincent Sidgwick.

These measurements were carried out by the methods described in our previous paper (T., 1913, **103**, 1959).

(1) *Conductivity.*

Kahlbaum's purest camphoric acid was recrystallised several times from conductivity water. The dilutions were mostly too great to admit of a calculation of the dissociation constant, especially in view of the fact that this is a dibasic acid; but the values have been calculated for those experiments in which the concentration was greater than 0·001 molar normal, where the second dissociation may be taken to have no effect. The conductivity of the water used was added, as described in the previous paper (*loc. cit.*, p. 1960).

Table I.

Conductivity of Camphoric Acid at 25°.

Molecular normality.	Specific conductivity.	Molecular normality.	Specific conductivity.	Dissociation constant.
0·0000964	0·01408	0·000698	0·04172	—
0·0001690	0·01864	0·000724	0·04249	—
0·0001885	0·02052	0·000878	0·04714	—
0·0003302	0·02838	0·001136	0·05428	0·00199
0·0004222	0·03205	0·001519	0·06327	0·00198
0·0004720	0·03371	0·001794	0·06956	0·00200
0·0005637	0·03782	0·001834	0·07006	0·00198
0·0006181	0·03901	0·002131	0·07578	0·00197

Conductivity of water, 1·3 gemmhos.
Mean K 0·00198. (μ_a=394·6.)

Table II.

Conductivity of Camphoric Acid at 18°.

Series.	Molecular normality.	Specific conductivity.	Series.	Molecular normality.	Specific conductivity.	Dissociation constant.
C	0·0000229	0·00564	*B*	0·0003436	0·02591	—
B	0·0000498	0·00839	*B*	0·0005160	0·03361	—
C	0·0000585	0·01004	*A*	0·0005458	0·03444	—
C	0·0001007	0·01429	*B*	0·0007092	0·04004	—
A	0·0001204	0·01488	*A*	0·0008457	0·04620	—
C	0·0001571	0·01749	*B*	0·001032	0·04879	0·00242
B	0·0001733	0·01856	*B*	0·001494	0·05901	0·00235
C	0·0002249	0·02128	*A*	0·001539	0·05987	0·00230
A	0·0003008	0·02537				

Conductivity of water in series *A*, 0·84 gemmhos.
" " " *B*, 1·38 "
" " " *C*, 1·45 "
Mean K 0·00236. (μ_a=342·9.)

(2) *Rate of Hydration.*

Kahlbaum's purest camphoric anhydride was recrystallised from a mixture of alcohol and water. The finely powdered solid was shaken for varying periods of time with water in the thermostat, and the solution filtered into the conductivity cell. The rate of hydration is extremely small. At 25° the reaction is complete in about a fortnight; at 18° the solution should be left for a month before the end-point is taken; but to expedite matters the cell was, in some cases, after the lapse of a fortnight, heated at 50° for some hours to complete the change. The extreme slowness of the reaction and the sparing solubility of the anhydride naturally diminish the accuracy of the measurements.

TABLE III.

Rate of Hydration of Camphoric Anhydride at 25°.

Final normality of acid.	Initial normality of anhydride.	No. of readings.	Maximum error per cent.	$k \times 10^4$.
0·000267	0·000258	48	6·6	1·58
0·000569	0·000556	26	5·4	1·59
0·001141	0·001096	26	3·3	1·55
0·001208	0·001206	49	4·5	1·60
0·001372	0·001346	60	3·0	1·60

Mean k 0·000158. (Maximum error 1·8 per cent.)

Half-life period, 31 hours 42 minutes.

TABLE IV.

Rate of Hydration of Camphoric Anhydride at 18°.

Final normality of acid.	Initial normality of anhydride.	No. of readings.	Maximum error per cent.	$k \times 10^4$.
0·000337	0·000277	17	5·7	1·00
0·000326	0·000286	24	4·8	0·98
0·000438	0·000415	36	4·8	0·99
0·000485	0·000448	31	4·3	0·93

Mean k 0·0000975. (Maximum error 4·7 per cent.)

Half-life period, 51 hours 30 minutes.*

$k_{25}/k_{18} = 1580 \div 975 = 1{\cdot}64$. Temperature-coefficient for 10°, 2·00.

* The quickest change which has been measured by this method is that of maleic anhydride (Rivett and Sidgwick, T., 1910, **97**, 1681). Its half-life period at 25° is 26·4 seconds; it thus reacts with water 4330 times as fast as camphoric anhydride at the same temperature, and 7100 times as fast as camphoric anhydride at 18°. This indicates the range of velocities over which the conductivity method is available.

(3) *Catalytic Action of Alkali.*

The extreme slowness with which this anhydride reacts suggested that it would be a convenient material for examining the influence of alkali on the rate of hydration. The direct method, measuring the rate of change of conductivity of a solution of the anhydride in alkali, did not seem feasible, mainly owing to the difficulty of keeping unchanged so dilute a solution of alkali as would be required. An indirect method was therefore used.

If an excess of the anhydride is shaken with water, it will dissolve, and the dissolved part will react with the water. This second change is so slow that one may expect the solution after a short time to be practically saturated with anhydride. When this point is reached the rate of formation of the acid will be constant (as long as sufficient excess of solid anhydride is present), being equal to the product of the concentration (solubility) and the velocity-constant. If the experiment is repeated with a solution of alkali instead of water, the rate of formation of the acid, which can be determined by titration, will still be proportional to this product, provided that the rate of solution is still sufficiently greater than that of hydration. The concentration of the anhydride will be the same in this case as in the first, since the solubility will not be affected by the presence of alkali. Thus the ratio of the rate of production of acid in alkaline solution to that in water will be the ratio of the velocity-constants in the two solutions.

In order to test the method, a conductivity cell was fitted with a stirrer, and filled with water, together with an excess of finely powdered anhydride. The conductivity was measured from time to time, the stirrer being stopped only at the moment when the measurement was being made. The cell stood in a thermostat at 25°. The value obtained for D_N/D_t, the increase of normality of acid per minute, was $0{\cdot}422 \times 10^{-6}$, as a mean of seven readings varying between 0·403 and 0·435. This value is the product of the solubility of the anhydride (S_{an}) and the velocity-constant of hydration, which at 25° is known to be 0·000158.

Hence

$$S_{an} = 0{\cdot}422 \times 10^{-6} \div 0{\cdot}000158 = 0{\cdot}00267 \text{ molecular normality.}$$

The anhydride was then stirred under similar conditions with $N/200$-alkali. Twenty-five c.c. of the liquid were withdrawn from time to time by means of a pipette fitted with a filter, and titrated with $N/200$-acid.

In five minutes the titre had fallen from 23·2 c.c. to 4·0 c.c., and in half-an-hour the liquid was practically neutral. Thus in five

minutes the normality of the acid produced had increased from 0 to 0·00207.

Hence $D_N/D_t = 0{\cdot}00207 \div 5 = 0{\cdot}000414.$

Hence $$\frac{\text{Velocity in presence of } N/200\text{-alkali}}{\text{Velocity in pure water}} = \frac{0{\cdot}000414}{0{\cdot}422 \times 10^{-6}}.$$

$$= 10{,}000 \text{ (approx.)}.$$

The values are only rough, but they suffice to show the enormous catalytic power of hydroxyl ions, and are in accordance with the results obtained by Orton and Jones (T., 1912, **101**, 1715) by an entirely different method. The theoretical bearing of this remarkable fact, that the rate of hydration is catalysed by hydroxyl but not by hydrogen ions, has already been discussed in our previous paper (T., 1913, **103**, 1968).

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OXFORD. [*Received, April 15th*, 1915.]

LXXII.—*The Distribution of Energy in the Radiation from the Uviol-glass Lamp.*

By ARTHUR JOHN ALLMAND.

A NUMBER of photochemical investigations have been carried out in the past, and will doubtless be carried out in the future, in which the Schott mercury Uviol-glass lamp is used as the source of radiation, monochromatic illumination, if aimed at, being obtained by the use of filters. In order to utilise fully the results of these investigations, a knowledge of the distribution of energy in the different parts of the spectrum of the lamp is necessary.

In default of direct determinations of this distribution, it has been assumed by some workers (Luther and Forbes, *J. Amer. Chem. Soc.*, 1909, **31**, 780; Plotnikov, *Zeitsch. physikal. Chem.*, 1912, **79**, 642) that the values obtained by Ladenburg (*Physikal. Zeitsch.*, 1904, **5**, 525; measurements of less value for this particular purpose were made by Pflüger, *Ann. Physik*, 1908, [iv], **26**, 789) for the quartz mercury lamp could be employed. Owing, however, to the greater transparency of quartz as compared with uviol-glass even for the less refrangible regions of the ultra-violet, it is unlikely, as was pointed out by Winther (*Zeitsch. Elektrochem.*, 1913, **19**, 395) and by Bruner (*ibid.*, 555) that calculations made on this basis are of any value.

The first attempt to measure directly the ratios in question for

the Uviol lamp we owe to Winther (*loc. cit.*), who employed the "fluorometer" designed by him. The following table contains in the first column the values for the intensities of certain bands of the quartz mercury lamp, referred to the blue band as unity. These values are taken from the graphical integration of Ladenburg's measurements carried out by Plotnikov ("Photochemische Versuchstechnik," 1912, 17—19). The second and third columns contain Winther's values for the quartz and uviol-glass lamps:

Band.	Quartz (L.)	Quartz (W.)	Uviol (W.)
436 $\mu\mu$	1·00	1·00	1·00
405	0·54	0·62	0·29
362	1·83	2·31	0·25
313	1·28	0·87	0·045
302	—	0·29	—
254	0·20	0·23	—

The agreement between Ladenburg's and Winther's ratios for the quartz lamp is, on the whole, exceedingly good. The biggest percentage deviation is shown in the case of the 362 $\mu\mu$ (ultraviolet) band. Plotnikov's integration of Ladenburg's figures for the 313 $\mu\mu$ band also includes the 302 $\mu\mu$ band, and one should strictly compare about two-thirds of his value of 1·28 (that is, 0·86) with Winther's figure of 0·87, or else the sum of Winther's values for the 313 $\mu\mu$ and 302 $\mu\mu$ bands (that is, 1·16) with his figure of 1·28. Winther's figures for the Uviol lamp indicate, as would be expected, that the intensities of the ultraviolet bands, compared with the blue band, are far less than for the quartz lamp, and also, which is more surprising, that the relative intensity of the violet band (405 $\mu\mu$) is also considerably less.

This is not the place to criticise the principle involved in Winther's method. Various figures given in the course of his interesting paper, as well as the ratios for the quartz lamp quoted above, show that it is capable of giving results of a very fair degree of accuracy in many cases. It may, however, be pointed out that the intensity of fluorescent light produced by his comparison standard source is strictly given by:

$$I' = \int_{\lambda_1}^{\lambda_2} k_\lambda I_\lambda 10^{-m_\lambda(5-d)}.$$

(where I' is the total intensity of fluorescent light, k_λ, I_λ, m_λ are respectively the fluorescence factor, intensity of the source, and extinction-coefficient for the wave-length λ; and λ_1 and λ_2 represent the limits of the spectrum capable of exerting fluorescence), and not by:

$$I' = kI10^{-m_n(5-d)}.$$

(where I is the [constant] total intensity of the comparison source,

and k and m_n are mean values for the fluorescence factor and the extinction-coefficient). The fact that one variable (m_n) occurs in the exponent, whereas the others do not, renders it in theory impossible to get a really satisfactory value of m_n, a magnitude essentially involved in all measurements made with the instrument. Winther quotes mean values of m_n, determined for various fluorescing solutions by measurements of the standard comparison source against monochromatic light of different wave-lengths, and it would be interesting to know how far the separate values thus obtained differ amongst themselves. Apart from this objection, the actual error in reading may amount to as much as 20 per cent. with weak sources of light (although this can be considerably reduced by repeated observations), and slight variations in the standard lamp may also prove of importance. Plotnikov (*Zeitsch. Elektrochem.*, 1913, **19**, 754) estimates the accuracy of the apparatus as 20—30 per cent. As it is particularly when measuring comparatively weak sources of radiation, the quality of which considerably differs from that of the comparison source, that we should expect these different factors to count, it seemed desirable to investigate the distribution of the energy in the Uviol lamp by an independent method.

The method chosen was that used by Ladenburg (*loc. cit.*) for the quartz lamp, namely, direct measurement of the intensity of the different bands by means of a thermopile. The Uviol lamp was burnt under constant conditions of current and voltage at some distance from a Hilger monochromatic illuminator, on the front slit of which an image of the lamp was thrown by means of a quartz lens. A large, water-cooled screen protected the instrument from direct radiation from the lamp, and the slit could be illuminated by means of a water-cooled shutter. The dispersed light passed through the second slit of the instrument on to a Hilger thermopile placed immediately behind it, the thermopile being short-circuited on to a Paschen galvanometer, the coils of which had the same resistance as that of the thermopile, namely, about three ohms. Unfortunately, the Paschen galvanometer, although exceedingly sensitive, and, owing to the lightness of its suspension, scarcely affected by incidental mechanical shaking, is very subject to external magnetic disturbances, and its design renders it difficult to shield effectually. Consequently, although it was almost completely surrounded by 5 cm. of soft iron wire wound on a vertical drum, with 2·5 cm. of transformer plates above and below, it was impossible to work with it in the daytime. All definitive measurements were carried out at night, and even then its sensitiveness had to be reduced to 10^{-1}—10^{-2} of its maximum value

to obtain a zero steady enough with which to work. Further, the low dispersion of the quartz prism of the monochromatic illuminator made it necessary to work with comparatively narrow front and back slits if the different bands after dispersion were to be completely separated. Thus the amount of energy entering the instrument was low, and the surface of the thermopile was only partly utilised, and these factors, combined with the low sensitivity of the galvanometer, resulted in very small deflexions, varying, according to width of slit, position of band, and sensitivity of galvanometer, between 0·8 and 50 mm., and being mostly less than 1 cm.

In order to measure such deflexions at all satisfactorily with a galvanometer the zero of which was continually changing, the readings had obviously to be repeated a large number of times. As two kinds of change of zero had to be contended with, namely, a gradual drift in one particular direction, and smaller changes occupying a fraction of a second, the method of measurement adopted was as follows: Six readings were taken at rapid and regular intervals with the shutter down. Their mean is denoted by Z_0. The shutter was then raised, and six more readings were taken in the same way, their mean being denoted by R_1. A cycle of twelve readings required about one minute. Six more readings of the zero were then taken (shutter down), their mean giving a value Z_1, and the procedure was repeated until twenty-one sets of six readings had been taken, the last set always being made with the shutter down, and the whole operation occupying about ten minutes. The values of the deflexions obtained under these conditions were given by:

$$R_1 - \left(\frac{Z_1 + Z_0}{2}\right) = D_1,$$

$$R_2 - \frac{(Z_2 + Z_1)}{2} = D_2,$$

$$R_{10} - \left(\frac{Z_{11} + Z_{10}}{2}\right) = D_{10},$$

and the mean of the different values of D was taken as representing the deflexion for the band in question. The extreme variation between the different values of D was about 50 per cent. with small, 15 per cent. with large deflexions, and the probable error in the final value of D varied between 5 and 20 per cent.

That this method is capable of giving satisfactory results is shown by the following figures obtained in different series of experiments:

Deflexion given by		Ratio of deflexions.
436 $\mu\mu$	313 $\mu\mu$	—
7·6 mm.	1·3 mm.	0·17
46·9	8·1	0·17
35·2	5·9	0·17

Deflexion given by		Ratio of deflexions.
436 $\mu\mu$	362 $\mu\mu$	
8·1 mm.	3·2 mm.	0·40
7·6	3·1	0·41
7·6	2·7	0·35
3·0	1·3	0·43

Most of the definitive measurements were carried out with a front slit of 0·4—0·5 mm. width and back slit 0·4—0·8 mm. For the ultraviolet bands it was possible to use wider slits, but the green and the yellow bands were only just separated with the narrowest slits used. The actual intensity ratios of yellow/blue and green/blue are to be looked on as merely preliminary. On the other hand, there is little doubt that the sum of the intensities of the green and the yellow bands is, as will be seen, substantially equal to the intensity of the blue band. Several experiments gave this result. In all cases, with the exception of the ultraviolet band 313 $\mu\mu$, the width of the band measured was taken from the diagram on p. 18 of Plotnikov's "Photochemische Versuchstechnik." The band specified was measured between the limits 300—320 $\mu\mu$.

The lamp used was run off the 230-volt mains in series with a resistance and an inductance. It usually took about an hour to attain constant values of current and voltage. Measurements were made with:

(*a*) 3·5 amperes and 56 volts,
(*b*) 3·2 amperes and 34 volts,

and practically identical values for the intensity ratios were obtained.

Column 1 of the following table contains the values finally obtained, referred to the intensity of the blue band as unity. Columns 2 and 3 contain respectively Winther's figures for the Uviol lamp and Ladenburg's figures for the quartz lamp:

	Uviol (A).	Uviol (W).	Quartz (L).
571$\mu\mu$	0·27	—	2·63
541	0·73	—	3·93
436	1·00	1·00	1·00
405	0·56	0·29	0·54
362	0·42	0·25	1·83
313	0·17	0·045	1·28 (0·86)

Comparing columns 1 and 2, the values for the three most refrangible bands are seen to be considerably greater than Winther's figures. Columns 1 and 3 lead to the conclusion that, whilst the relative intensities of the blue and the violet bands are the same in the quartz and the uviol-glass lamps, and the relative intensities of the ultraviolet bands far less for the Uviol lamp, this last statement also holds good for the green and the yellow bands, which is an unforeseen result.

It remains to apply, if possible, the above figures to already existing photochemical data obtained with the Uviol lamp. This can only be done approximately and with a great deal of uncertainty. Spencer (T., 1914, **105**, 2572), who made use of Winther's light-filters and Winther's figures for the distribution of energy, points out that the velocity of decomposition of a sodium hypochlorite solution for a given intensity of light appears to be greater the shorter the wave-length of the active radiation. Assuming that Winther's filters are correct (which is at all events approximately true), and that the three thicknesses of Uviol glass used between the lamp and the hypochlorite solution did not selectively affect the intensities of the different bands (this is less likely to be correct), the ratios of the velocity-coefficients obtained become:

436$\mu\mu$	1·0 (1·0)
405	2·2 (4·3)
362	4·3 (7·1)
313	4·4 (16·3)

Spencer's values are bracketed. The absolute values of the ratios are considerably altered, but the order remains unchanged.

It has been proposed by Bruner (*loc. cit.*) that the velocity of a photochemical reaction is proportional to the energy absorbed, and independent of the frequency of the light. Certain experiments by Lasareff (*Ann. Physik.*, 1907, [iv], **24**, 661) on the bleaching of organic dyes appear to support this view; others (*ibid.*, 1912, [iv], **37**, 812) by the same author are not in accord with it. This last statement also holds good of the experiments of Henri and Wurmser (*Compt. rend.*, 1913, **156**, 3) on the action of ultraviolet light on acetaldehyde. Bruner attempted to show that experiments of Plotnikov (*Zeitsch. physikal. Chem.*, 1912, **79**, 641) on the photochemical addition of bromine to cinnamic acid agree with his view. In the opinion of the present writer too many assumptions and approximations are involved to justify any conclusions drawn from those experiments. The only experimental work that can be utilised with advantage in this connexion is the investigation of the photochemical oxidation of quinine by chromic acid carried out by Luther and Forbes (*loc. cit.*). Assuming complete absorption of the 406 $\mu\mu$ and 362 $\mu\mu$ bands, these workers found the ratios of the velocity-constants to be:

$$\frac{k_{406}}{k_{362}} = \frac{1{\cdot}00}{0{\cdot}82}.$$

The figures obtained in the present paper indicate:

$$\frac{i_{406}}{i_{362}} = \frac{1{\cdot}00}{0{\cdot}75}.$$

The agreement is good, and the discrepancy certainly not greater than the various experimental errors involved.

The author would finally point out the importance of knowing, and, if necessary, measuring, the extinction-coefficients, not only of the different liquid and gaseous systems on which the action of light is being studied, but also of the materials of the vessels containing such systems. Photochemical measurements carried out without a knowledge of these magnitudes and without tried and suitable filters to secure essentially monochromatic light lose the greater part of their value.

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[*Received, April 6th*, 1915.]

LXXIII.—*Derivatives of 2-Pyridylhydrazine and 2-Quinolylhydrazine.*

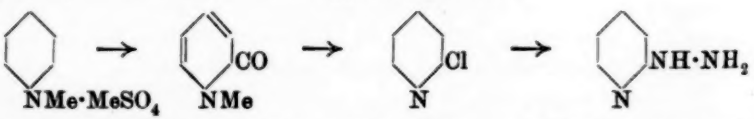
By ROBERT GEORGE FARGHER and REGINALD FURNESS.

DURING the course of their experiments on harmine and harmaline Perkin and Robinson (T., 1913, **103**, 1974) prepared acetone-2-quinolylhydrazine with the object of converting it into 2-methyl-12-quinindole by Fischer's method.

It was found that the quinindole derivative was not produced by heating with hydrochloric acid, zinc chloride, or other condensing agents, because hydrolysis occurred in most of the experiments.

Since it is important to determine whether the process is generally inapplicable to the pyridine nucleus, we have carried out, at the suggestion of Professor Perkin, a further series of experiments with derivatives of 2-pyridylhydrazine and 2-quinolylhydrazine.

2-Pyridylhydrazine does not appear to have been previously described, but we have found that it can be readily prepared by the following series of reactions. Pyridine methosulphate is oxidised by potassium ferricyanide to 1-methyl-2-pyridone, which, when heated with phosphorus pentachloride and phosphoryl chloride, yields 2-chloropyridine, and this, on boiling with hydrazine hydrate, is converted into 2-pyridylhydrazine:

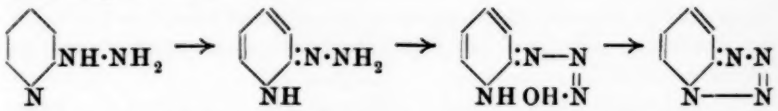


2-Pyridylhydrazine melts at 46°, distils at 140°/20 mm., and

combines with aldehydes and ketones in the same manner as phenylhydrazine.

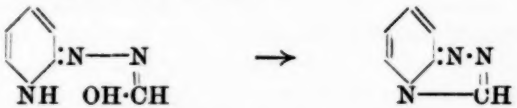
Ethyl acetoacetate combines readily with 2-pyridylhydrazine with the formation of the hydrazone, and this, when distilled under diminished pressure, loses ethyl alcohol with the formation of 1-(2′-pyridyl)-3-methyl-5-pyrazolone (m. p. 110°).

When 2-pyridylhydrazine is heated with nitrous acid an interesting change takes place, and 1:2:3:9-benzo*iso*tetrazole is formed according to the scheme:



It melts at 159°, and explodes when touched with a red-hot rod.

1:2:9-Benzo*iso*triazole is obtained when 2-pyridylhydrazine is heated with anhydrous formic acid:



and is a crystalline mass, which yields a platinichloride,

$$(C_6H_5N_3)_2,H_2PtCl_6,$$

and a characteristic explosive silver nitrate derivative,

$$C_6H_5N_3,AgNO_3.$$

2-Quinolylhydrazine was first obtained by Marckwald and Meyer (*Ber.*, 1900, **33**, 1885) from 2-chloroquinoline and hydrazine hydrate.

Perkin and Robinson (T., 1913, **103**, 1978) have described a modification of the original method, which allows of considerable quantities of 2-quinolylhydrazine being prepared with comparatively little trouble. The hydrazine separates from water in orange crystals, and melts at 142—143°.

2-Quinolylhydrazine combines readily with ethyl acetoacetate, and the resulting hydrazone (m. p. 90°) when heated on the steam-bath loses ethyl alcohol with the formation of 1-(2′-quinolyl)-3-methyl-5-pyrazolone, a crystalline substance which melts at 140°.

Many attempts have been made to convert derivatives of 2-pyridylhydrazine and 2-quinolylhydrazine into pyrindole and quinindole derivatives by the action of zinc chloride, hydrochloric acid, and other agents for the removal of ammonia, but always without success, so that it appears unlikely that such substances can be obtained in the pyridine series by reactions analogous to those which work so well in the benzene series.

One of the reasons which led us to undertake this investigation

and to prepare so many derivatives of 2-pyridylhydrazine and 2-quinolylhydrazine was the prospect that these substances might exhibit interesting physiological properties. This matter is being investigated.

Experimental.

1-*Methylpyridone.*

1-Methylpyridone was first prepared by Decker (*J. pr. Chem.*, 1911, [ii], **84**, 436), and more recently by Fischer and Neundlinger (*Ber.*, 1913, **46**, 2554). In preparing considerable quantities of the substance we have employed the following modification of Decker's method.

To potassium ferricyanide (195 grams) dissolved in water (400 c.c.) and well cooled in ice, are added, drop by drop from separate funnels, potassium hydroxide (50 grams) in water (60 c.c.), and pyridine methosulphate (53 grams), diluted to 60 c.c. with water. The mixture is mechanically stirred during the addition and for about half-an-hour afterwards; the potassium ferrocyanide, which crystallises, is filtered off, the filtrate is saturated with potassium hydroxide, and the oil which separates is extracted with ether, dried, and distilled, when 1-methylpyridone is obtained as a bright yellow oil boiling at 259°. The yield varies between 90 and 95 per cent. of that theoretically possible.

2-*Chloropyridine.*

2-Chloropyridine was obtained by O. Fischer (*Ber.*, 1898, **31**, 611; 1899, **32**, 1298; compare Pechmann and Baltzer, *Ber.*, 1891, **24**, 3150) by the action of a mixture of phosphorus pentachloride and phosphoryl chloride on 1-methylpyridone. We have found, however, that if more of the phosphoryl chloride and less of the pentachloride are used than Fischer recommends, the yield is much better.

1-Methylpyridone (26 grams) is heated in a Geissler flask with a mixture of phosphoryl chloride (40 grams) and phosphorus pentachloride (60 grams) for nine hours at 150—160°. The excess of phosphoryl chloride is distilled off under diminished pressure, and the residue is carefully decomposed with water, made strongly alkaline with sodium hydroxide, and distilled with steam. 2-Chloropyridine, extracted from the distillate with ether, dried over potassium hydroxide, and distilled, boils at 170° (uncorr.), and the yield is almost theoretical.

2-*Pyridylhydrazine*, $C_5H_4N{\cdot}NH{\cdot}NH_2$.

2-Pyridylhydrazine is readily obtained when 2-chloropyridine is heated to boiling with an excess of hydrazine hydrate, and when the following conditions are observed no hydrazopyridine appears to be produced.

2-Chloropyridine (34 grams) is boiled with hydrazine hydrate (140 grams) for four hours on a sand-bath, and, after cooling, the whole is extracted with ether (*A*), which dissolves a considerable part of the 2-pyridylhydrazine and some unchanged 2-chloropyridine. Hydrazine hydrate, hydrazine hydrochloride, and 2-pyridylhydrazine hydrochloride remain in the residue. The excess of hydrazine hydrate is distilled under diminished pressure, and the residue is treated with concentrated potassium hydroxide and extracted with ether (*B*). The extracts *A* and *B* are united, dried over potassium hydroxide, and evaporated, and the residue is fractionated under diminished pressure, when 21 grams of 2-pyridylhydrazine and 12 grams of unchanged 2-chloropyridine are obtained:

0·0892 gave 0·1805 CO_2 and 0·0529 H_2O. C = 55·2; H = 6·6.
0·0520 „ 17·1 c.c. N_2 at 16° and 764 mm. N = 38·5.
$C_5H_7N_3$ requires C = 55·05; H = 6·4; N = 38·5 per cent.

2-*Pyridylhydrazine* boils at 185°/140 mm., 170°/55 mm., 145°/25 mm., and 140°/20 mm., and when pure readily solidifies to a white, crystalline mass, melting at about 46°, which may be recrystallised from light petroleum. It decomposes rapidly on exposure to the air, and an intense odour of pyridine is noticeable; it can be kept indefinitely in sealed tubes. Towards picric acid and platinic chloride it behaves as a monacid base; it reduces Fehling's solution.

The *picrate*, which is insoluble in water, separates from alcohol in slender needles, and melts and decomposes at 160—161°:

0·0962 gave 20·5 c.c. N_2 at 18° and 772 mm. N = 25·0.
$C_5H_7N_3,C_6H_3O_7N_3$ requires N = 24·9 per cent.

A pale yellow precipitate of the *platinichloride* is obtained when platinic chloride is added to the aqueous solution of the hydrochloride of the base. It blackens at 160°, and melts and decomposes at 256°:

0·1046 gave 0·0326 Pt. Pt = 31·16.
$(C_5H_7N_3)_2,H_2PtCl_6$ requires Pt = 31·05 per cent.

Acetaldehyde-2-pyridylhydrazone, $C_5H_4N{\cdot}NH{\cdot}N{:}CHMe$.

In the preparation of this substance freshly distilled acetaldehyde (1 gram) is added drop by drop to a solution of 2-pyridylhydrazine (2 grams) in ether, when a vigorous reaction ensues. After evaporation of the ether the solid residue is drained on porous porcelain, and then recrystallised from aqueous alcohol or light petroleum, from which it separates in needles, melting at 70°:

0·1074 gave 29·6 c.c. N_2 at 17° and 740 mm. N = 31·1.

$C_7H_9N_3$ requires N = 31·1 per cent.

The addition of a trace of potassium hydroxide to the alcoholic solution of the hydrazone causes the development of a pink colour, which is discharged by acids and regenerated by excess of the alkali. Crystallisation from water or aqueous alcohol containing a trace of potassium hydroxide does not appreciably affect the melting point.

Benzaldehyde-2-pyridylhydrazone, $C_5H_4N{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$.

This derivative is obtained when 2-pyridylhydrazine (2 grams), dissolved in dilute acetic acid, is mixed with benzaldehyde (2 grams); the condensation product separates immediately. It is recrystallised from alcohol, from which it separates in long, glistening, colourless needles, melting at 148°:

0·1596 gave 29·5 c.c. N_2 at 18° and 760 mm. N = 21·3.

$C_{12}H_{11}N_3$ requires N = 21·3 per cent.

Acetone-2-pyridylhydrazone, $C_5H_4N{\cdot}NH{\cdot}N{:}CMe_2$.

2-Pyridylhydrazine (8 grams) is dissolved in acetone and kept for some time; the excess of solvent is removed, water added, and the product extracted with ether, dried over calcium chloride, and fractionated under diminished pressure.

Acetone-2-pyridylhydrazone crystallises from light petroleum in rhombic prisms melting at 73°; it boils at 145°/25 mm., 160°/35 mm., and 180°/70 mm. It dissolves readily in alcohol, chloroform, benzene, or toluene, and in cold dilute acids, from which it is precipitated by the addition of alkali:

0·1404 gave 33·8 c.c. N_2 at 14° and 750 mm. N = 28·0.

$C_8H_{11}N_3$ requires N = 28·2 per cent.

Many attempts were made to prepare a pyrindole derivative, but without success. The finely divided hydrazone, intimately mixed with a large excess of zinc chloride, was heated at temperatures varying between 170° and 300°; on dissolving the fusion in water,

adding sodium hydroxide, and extracting with ether, much unchanged hydrazone was obtained, and it was evident that no pyrindole formation had taken place. Similar results were obtained when dilute or concentrated acids were used, under pressure, in the place of zinc chloride.

Acetophenone-2-pyridylhydrazone, $C_5H_4N\cdot NH\cdot N{:}CMe\cdot C_6H_5$.

This derivative is prepared by keeping molecular quantities of acetophenone and 2-pyridylhydrazine for some time in alcoholic solution. Water is then added, and the product is collected and recrystallised from dilute alcohol, from which it separates in colourless crystals melting at 90°:

0·1467 gave 26·0 c.c. N_2 at 18° and 743 mm. N = 20·0.

$C_{13}H_{13}N_3$ requires N = 19·9 per cent.

The 2-Pyridylhydrazone of Pyruvic Acid, $C_5H_4N\cdot NH\cdot N{:}CMe\cdot CO_2H$.

The reaction between 2-pyridylhydrazine and pyruvic acid proceeds with almost explosive violence. Pyridylhydrazine (2 grams) dissolved in ether is gradually added to pyruvic acid (1·7 grams), when an extremely vigorous reaction ensues, and the condensation product separates immediately. It is triturated with ether, collected, and crystallised from aqueous alcohol, from which it separates in long needles, containing $1\frac{1}{2}$ molecules of water of crystallisation. It melts at 188° with evolution of carbon dioxide, and dissolves in both acids and alkalis. It is fairly soluble in hot water, and sparingly so in benzene or chloroform. Using the conditions described in the case of acetone-2-pyridylhydrazone, we were unable to induce pyrindole formation:

0·1165 lost 0·0153 at 100°. H_2O = 13·1.

After dehydration, 0·1010 gave 21·0 c.c. N_2 at 19° and 750 mm. N = 23·6.

$C_8H_9O_2N_3$ requires N = 23·5 per cent.

$C_8H_9O_2N_3,1\frac{1}{2}H_2O$ requires H_2O = 13·1 per cent.

The 2-Pyridylhydrazone of Ethyl Pyruvate, $C_5H_4N\cdot NH\cdot N{:}CMe\cdot CO_2Et$.

This ester is obtained when the acid is esterified by boiling with alcohol and sulphuric acid, but is best prepared by mixing 2-pyridylhydrazine (2·2 grams) with ethyl pyruvate (2·3 grams) in alcoholic solution. After a short time the product is precipitated by the addition of water, and recrystallised from aqueous alcohol, from

which it separates in slender needles, containing one molecule of water of crystallisation, and melting at 53°. From light petroleum it crystallises in the anhydrous condition; it then melts at 74°.

I. Crystals from dilute alcohol:

0·1053 gave 17·3 c.c. N_2 at 17° and 744 mm. N = 18·7.

$C_{10}H_{13}O_2N_3,H_2O$ requires N = 18·7 per cent.

The same specimen after drying over phosphoric oxide:

0·1076 gave 19 c.c. N_2 at 18° and 760 mm. N = 20·4.

II. Crystals from light petroleum:

0·1333 gave 24·5 c.c. N_2 at 17° and 750 mm. N = 20·7.

$C_{10}H_{13}O_2N_3$ requires N = 20·3 per cent.

Acetyl-2-pyridylhydrazine, $C_5H_4N{\cdot}NH{\cdot}NH{\cdot}COMe$.

In the preparation of this substance, acetic anhydride (1 gram) is carefully added to 2-pyridylhydrazine (2·2 grams). Much heat is developed, and, after cooling, the hard mass is triturated with ether to remove the excess of either component, when a white solid is obtained, which is soluble in cold water, alcohol, or chloroform, but dissolves very sparingly in benzene. It separates from the latter solvent in twin prisms, which melt at 150°:

0·1164 gave 28·1 c.c. N_2 at 15° and 750 mm. N = 27·9.

$C_7H_9ON_3$ requires N = 27·8 per cent.

Phthalyl-2-pyridylhydrazide, $\begin{matrix}C_6H_4\\ CO{-}O\end{matrix}\!\!>\!C{:}N{\cdot}NH{\cdot}C_5H_4N$.

The hydrazide is obtained when molecular quantities of 2-pyridylhydrazine and phthalic anhydride are heated together in alcoholic solution for two hours, and the product cooled. It crystallises from alcohol in colourless, rhombic prisms, which melt at 208°:

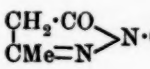
0·1028 gave 15·7 c.c. N_2 at 19° and 764 mm. N = 17·7.

$C_{13}H_9O_2N_3$ requires N = 17·6 per cent.

2-Pyridylsemicarbazide, $C_5H_4N{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$.

2-Pyridylsemicarbazide is readily obtained when 2-pyridylhydrazine, dissolved in sufficient dilute hydrochloric acid to form the monohydrochloride, is treated with an equivalent quantity of potassium cyanate in aqueous solution and the mixture is warmed on the water-bath for half-an-hour. On cooling, the semicarbazide separates in granular form; it melts, after recrystallisation from hot water, at 186°. It dissolves readily in alcohol, hot water, and acids:

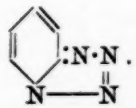
0·0634 gave 20·1 c.c. N_2 at 18° and 762 mm. N = 36·7.
$C_6H_8ON_4$ requires N = 36·8 per cent.

1-(2′-*Pyridyl*)-3-*methyl*-5-*pyrazolone*,  .

In preparing this substance, the following method was found to give the best results. Ethyl acetoacetate (5·2 grams) is mixed with 2-pyridylhydrazine (4·4 grams), when water soon separates. The hydrazone is then dissolved in ether, dried, and distilled under diminished pressure, whereby ethyl alcohol is eliminated and the pyrazolone distils in almost quantitative yield:

0·0594 gave 12·3 c.c. N_2 at 18° and 760 mm. N = 23·9.
0·1425 „ 0·3237 CO_2 and 0·0710 H_2O. C = 61·9; H = 5·5.
$C_9H_9ON_3$ requires C = 61·7; H = 5·14; N = 24·0 per cent.

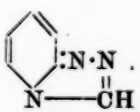
The compound is sparingly soluble in cold water, but dissolves readily in alcohol or toluene. After recrystallisation from dilute alcohol or light petroleum, it melts at 110°. Its aqueous solution gives a blue coloration with ferric chloride.

1 : 2 : 3 : 9-*Benzoisotetrazole*,  .

This substance is obtained when 2-pyridylhydrazine (1 gram), dissolved in dilute acetic acid (50 per cent.) and cooled in a freezing mixture, is treated with a solution of sodium nitrite (0·8 gram $NaNO_2$). After a short time crystals are deposited, which, after being collected and washed, are quite pure, and melt at 159°:

0·0668 gave 26·6 c.c. N_2 at 18° and 771 mm. N = 46·7.
$C_5H_4N_4$ requires N = 46·7 per cent.

The compound crystallises in colourless, elongated prisms, which are almost insoluble in cold water or ether, but soluble in warm water, alcohol, or acetone. When touched with a red-hot rod it decomposes explosively.

1 : 2 : 9-*Benzoisotriazole*,  .

This substance was prepared by the condensation of 2-pyridylhydrazine and formic acid. 2-Pyridylhydrazine (1 gram) is boiled with an excess of formic acid (4 grams) during an hour, the excess of the acid is evaporated, and the residue is placed in a vacuum desiccator; it gradually solidifies to a white, crystalline mass, which

is extremely hygroscopic and retains water even when exposed over sulphuric acid for some hours. In order to characterise the substance, the compounds with platinic chloride and with silver nitrate were prepared, since, like naphthatriazole (Marckwald and Meyer, *Ber.*, 1900, **33**, 1885), it has the property of forming double compounds with many metallic salts.

The *platinichloride*, prepared in the usual way, is a light yellow, crystalline substance, which does not melt at 300°:

0·1421 gave 0·0430 Pt. Pt = 30·2.

$(C_6H_5N_3)_2,H_2PtCl_6$ requires Pt = 30·1 per cent.

The *silver nitrate* derivative is immediately precipitated when a solution of silver nitrate is added to the aqueous solution of the base. It crystallises from hot water in slender needles, which decompose at 228° when heated in a capillary tube, but explode when heated in larger quantity:

0·1343 gave 0·0497 Ag. Ag = 37·0.

$C_6H_5N_3,AgNO_3$ requires Ag = 37·2 per cent.

s-2-*Pyridyl*-2-*quinolylhydrazine*, $C_9H_6N{\cdot}NH{\cdot}NH{\cdot}C_5H_4N$.

This substance is readily obtained by the interaction of 2-chloroquinoline and 2-pyridylhydrazine, either without a solvent or in the presence of a tertiary base, such as pyridine. Molecular proportions of the two substances, dissolved in an excess of pyridine, are warmed during about an hour, after which the pyridine and pyridine hydrochloride are removed from the mixture by treatment with water. The yellow residue is recrystallised from alcohol, from which it separates in colourless crystals melting at 177°.

2-*Pyridyl*-2-*quinolylhydrazine* is very sparingly soluble in water or light petroleum, but fairly readily so in boiling alcohol. By oxidation with nitrous acid in acetic acid it yields the corresponding azo-compound:

0·0942 gave 19·7 c.c. N_2 at 16° and 746 mm. N = 23·9.

$C_{14}H_{12}N_4$ requires N = 23·7 per cent.

Acetaldehyde-2-*quinolylhydrazone*, $C_9H_6N{\cdot}NH{\cdot}N{:}CHMe$.

Acetaldehyde and 2-quinolylhydrazine combine readily at the ordinary temperature with the evolution of much heat, so that the reaction is best carried out in the presence of a diluent.

2-Quinolylhydrazine (2 grams) is powdered very finely, and made into a paste with a little alcohol. Acetaldehyde (2 grams) is then added drop by drop, the mixture being cooled during the addition. After a few minutes the mass becomes homogeneous, and then begins to deposit well-defined crystals, which are collected and

recrystallised from alcohol, when they are obtained in slender, colourless, silky needles, melting at 151°:

0·1052 gave 20·7 c.c. N_2 at 18° and 762 mm. N = 22·8.

$C_{11}H_{11}N_3$ requires N = 22·7 per cent.

The addition of a trace of potassium hydroxide to the solvent used for the recrystallisation had no appreciable effect on the melting point (compare Laws and Sidgwick, T., 1911, **101**, 2085). The presence of a trace of hydrochloric acid caused a slight lowering in the melting point, but this may have been due to the formation of a trace of the hydrochloride, although we could not detect chlorine in the product. It was noticed that when a drop of potassium hydroxide solution was added to the dilute alcoholic solution of the hydrazone an intense pink colour gradually developed, which was discharged on acidifying, and regenerated immediately on basifying.

Acetophenone-2-quinolylhydrazone,* $C_9H_6N\cdot NH\cdot N{:}CMe\cdot C_6H_5$.

When a solution of molecular proportions of acetophenone and 2-quinolylhydrazine in acetic acid is kept, yellow needles are deposited, which, after recrystallisation from alcohol, melt at 122°:

0·1213 gave 16·8 c.c. N_2 at 15° and 756 mm. N = 16·2.

$C_{17}H_{15}N_3$ requires N = 16·0 per cent.

The 2-Quinolylhydrazone of Pyruvic Acid,*

$C_9H_6N\cdot NH\cdot N{:}CMe\cdot CO_2H$.

When molecular quantities of pyruvic acid and quinolylhydrazine are mixed in ethereal solution the condensation product immediately separates as a yellow precipitate, which is very sparingly soluble in all the ordinary solvents. On heating, it darkens at 170°, and decomposes at 200°, with the evolution of carbon dioxide and ammonia:

0·1126 gave 17·8 c.c. N_2 at 17° and 760 mm. N = 18·2.

$C_{12}H_{11}O_2N_3$ requires N = 18·3 per cent.

The hydrazone was found to esterify readily when boiled with alcohol and sulphuric acid; the resulting *ester* melts at 134°:

0·1065 gave 15·0 c.c. N_2 at 14° and 760 mm. N = 16·5.

$C_{14}H_{15}O_2N_3$ requires N = 16·3 per cent.

Several attempts were made to induce quinindole formation, both by heating with zinc chloride at temperatures up to 300°, and with hydrochloric acid in sealed tubes. After heating with hydrochloric acid at 180—200° under pressure during four hours, and allowing

* This compound was prepared by Mr. Eric Robinson.

the tube to cool, long, silky needles separated, which, recrystallised from water, melted at 195°. The substance, which was insoluble in sodium carbonate, but soluble in sodium hydroxide, proved to be carbostyril (Found, C = 74·2; H = 4·9; N = 10·3. Calc., C = 74·5; H = 4·8; N = 9·7 per cent.)

*The 2-Quinolylhydrazone of Laevulic Acid,** $C_9H_6N\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CH_2\cdot CO_2H$.

A yellow precipitate of this derivative is immediately obtained when alcoholic solutions of 2-quinolylhydrazine and lævulic acid are mixed. After recrystallisation from boiling alcohol, in which it is only sparingly soluble, it melts and decomposes at 200°:

0·1419 gave 19·5 c.c. N_2 at 14° and 760 mm. N = 16·3.
$C_{14}H_{15}O_2N_3$ requires N = 16·3 per cent.

*Acetyl-2-quinolylhydrazine,** $C_9H_6N\cdot NH\cdot NH\cdot CO\cdot CH_3$.

This derivative is obtained when acetic anhydride (1 mol.) is added to 2-quinolylhydrazine (2 mols.), and the mixture stirred with a glass rod until it sets to a hard mass. This is triturated with ether to remove impurities, and recrystallised from alcohol, from which it separates in clusters of elongated, rhombic prisms, melting at 195°:

0·0630 gave 11·4 c.c. N_2 at 16° and 754 mm. N = 20·9.
$C_{11}H_{11}ON_3$ requires N = 20·9 per cent.

Benzoyl-2-quinolylhydrazine, $C_9H_6N\cdot NH\cdot NH\cdot CO\cdot C_6H_5$.

This derivative may be prepared by the action of either benzoic anhydride or benzoyl chloride on 2-quinolylhydrazine.

Molecular proportions of benzoic anhydride and 2-quinolylhydrazine are dissolved in alcohol and heated to boiling during two hours. The sparingly soluble hydrazine separates almost completely on cooling, and is collected and recrystallised from hot acetone, from which it is obtained in clusters of colourless needles melting at 204°. It is sparingly soluble in water, alcohol, acetone, or benzene:

0·1161 gave 16·3 c.c. N_2 at 19° and 764 mm. N = 16·2.
$C_{16}H_{13}ON_3$ requires N = 16·0 per cent.

Succinyl-2-quinolylhydrazide, $\begin{matrix}CO\text{——}O\\ |\\ CH_2\cdot CH_2\end{matrix}>C{:}N\cdot NH\cdot C_9H_6N$.

This derivative is obtained when equivalent quantities of 2-quinolylhydrazine and succinic anhydride, dissolved in alcohol,

* This compound was prepared by Mr. Eric Robinson.

are mixed and warmed on the water-bath during two hours. The hydrazide separates on cooling, and after recrystallisation from alcohol is obtained in pale yellow rhombs, which melt at 160° and decompose at a slightly higher temperature:

0·1392 gave 21·0 c.c. N_2 at 18° and 764 mm. N = 17·5.

$C_{13}H_{11}O_2N_3$ requires N = 17·4 per cent.

Phthalyl-2-quinolylhydrazide, $\begin{matrix} C_6H_4 \\ | \\ CO-O \end{matrix}\!\!>\!C{:}N\cdot NH\cdot C_9H_6N.$

The phthalylhydrazide of 2-quinolylhydrazine is obtained by boiling together molecular quantities of phthalic anhydride and 2-quinolylhydrazine in alcoholic solution during two hours. The hydrazide separates on cooling, and is collected and recrystallised from alcohol, from which it is deposited in pale orange plates melting at 236°:

0·1810 gave 22·9 c.c. N_2 at 17° and 744 mm. N = 14·3.

$C_{17}H_{11}O_2N_3$ requires N = 14·5 per cent.

The 2-Quinolylhydrazone of Ethyl Acetoacetate,
$C_9H_6N\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et.$

Equimolecular proportions of 2-quinolylhydrazine and ethyl acetoacetate are mixed and kept overnight. The resulting solid mass is spread on porous porcelain, and recrystallised from light petroleum, from which it separates in colourless needles melting at 90°:

0·1456 gave 20·3 c.c. N_2 at 19° and 743 mm. N = 15·6.

$C_{15}H_{17}O_2N_3$ requires N = 15·5 per cent.

1-(2′-*Quinolyl*)-3-*methyl*-5-*pyrazolone*, $\begin{matrix} CH_2\cdot CO \\ | \\ CMe{=}N \end{matrix}\!\!>\!N\cdot C_9H_6N.$

In order to obtain this derivative, the ester just described is warmed on the water-bath until the liquid mass solidifies to a hard cake; this dissolves fairly readily in boiling alcohol, and, on cooling, a voluminous mass of fluffy needles, melting at 140°, is obtained:

0·1710 gave 28·2 c.c. N_2 at 18° and 750 mm. N = 18·8.

$C_{13}H_{11}ON_3$ requires N = 18·7 per cent.

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[*Received, April 13th*, 1915.]

LXXIV.—*Enantiomorphism of Molecular and Crystal Structure.*

By William Barlow and William Jackson Pope.

In a recent paper on this subject (T., 1913, **103**, 837), Barker and Marsh draw a conclusion which, if accepted, finds important bearings in connexion with the stereochemical configurations of a number of inorganic substances. They conclude (p. 842) that "any assemblage of points possessing no other screw axes save digonal can only be endowed with optical activity providing the points themselves (that is, the molecules) are enantiomorphous"; as they state, this conclusion attributes enantiomorphism of configuration to the individual molecules of certain inorganic compounds, such as magnesium sulphate, $MgSO_4,7H_2O$, and others which are optically active in the crystalline condition.

The relation between optical activity and crystal structure has been discussed by Pope (T., 1896, **69**, 971) and by Barlow (*Phil. Mag.*, 1897, [v], **43**, 110); as our conclusions are incompatible with those of Barker and Marsh, we may supplement our previous work by a few remarks on that of these later authors.

Barker and Marsh state (p. 841) that the theory of crystal structure demands that, in cases of enantiomorphous grouping of non-enantiomorphous molecules, "the arrangement of molecules must possess screw axes of symmetry"; if this statement implies that the existence of these axes is a geometrical necessity in all such cases, it is incorrect. An enantiomorphous arrangement of non-enantiomorphous molecules is geometrically possible in any one of the sixty-five types of homogeneous arrangement discriminated by Sohncke; this is easily perceived if an example of each type is generated by applying the coincidence movements characteristic of it to some fortuitously-orientated, non-enantiomorphous unit, which is not a sphere or a mere point. Of the sixty-five types the first is destitute of axes of symmetry, and many possess only axes of rotation. Whilst a geometrical study of the Sohncke types of homogeneous arrangement demonstrates the incorrectness of Barker and Marsh's statement, its inherent improbability is rendered immediately obvious by a very simple consideration; the symmetry presented by a crystal structure is often manifestly derivable by some deformation from a higher symmetry, and it is clearly unlikely that a lowering of the symmetry which leads to the abolition of digonal screw axes would cause the destruction of the enantiomorphism.

The conclusion that "any assemblage of points possessing no other screw axes save digonal can only be endowed with optical activity providing the points themselves (that is, the molecules) are enantiomorphous," is fallacious. An error appears to have arisen from attributing the plane of symmetry characteristic of a single digonal point spiral, composed of one set of similarly placed points, to the space contained within the spiral; it is overlooked that the system may be a complex one in which a number of different point spirals having a common axis are found interpenetrating. The result of this interpenetration is, generally, that the compound spiral has a lower symmetry than that presented by a single component spiral, and is destitute of a plane of symmetry. In our recent joint work (T., 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528; 1910, **97**, 2308) we have always assumed that two or more distinct kinds of centres of atomic force are to be distinguished in the crystal structures of compound substances, and many years ago Sohncke foresaw that a number of interpenetrating regular point systems must, in some cases, be taken to represent the crystal structure; the justice of our assumption has now been completely established by the *X*-ray methods of exploring crystal structure. The experimental demonstration of the interpenetration of point systems representing the several kinds of atoms in a crystal structure quite destroys a line of argument based on the configuration of a single digonal spiral of points taken alone.

The following conclusion, diametrically opposed to that reached by Barker and Marsh, is true: If the enantiomorphism of a crystal structure and the consequent optical activity are entirely traceable to an arrangement of points (centres of force), located by coincidence movements about screw axes, the configuration of a single component molecule is not enantiomorphous. For, if it were, a molecule must contain more than one of the points of a single spiral, and if two points *A* and *B* of the same molecule are connected by the screw movement of this spiral, this movement will locate a succession of points, *A*, *B*, *C*, *D*, *E*, etc., all lying on a single spiral, and so related that *C* has the same relation to *B* that *B* bears to *A*, and so on. Consequently, if *A* and *B* are found within the same molecule, *C*, *D*, *E*, etc., will also be contained in it, and thus one dimension of the molecule will be infinite. Since this is impossible, no two points in the same molecule can, in geometrical strictness, be connected by a coincidence movement about a screw axis, and the presence of such an axis cannot be the origin of an enantiomorphous configuration of the molecule.

It is thus shown that, contrary to the conclusions drawn by

Barker and Marsh, no theoretical reasons at present exist for attributing enantiomorphous molecular configurations to those compounds which are optically active in the crystalline condition, but optically inactive in solution.

THE CHEMICAL LABORATORY,
CAMBRIDGE UNIVERSITY. [*Received, April 13th,* 1915.]

LXXV.—*The Racemisation of Phenyl-*p*-tolylacetic Acid.*

By ALEX. McKENZIE and SIBYL TAITE WIDDOWS.

IT is well known that alkali often causes an interchange of groupings to occur in an optically active system. The catalytic racemisation thus induced, either partial or incomplete as the case may be, is accelerated by an elevation of temperature in such cases where the latter effect has actually been examined; for example, a solution of *l*-mandelic acid in potassium hydroxide is comparatively stable at the ordinary temperature so far as its rotatory power is concerned, even when the amount of the base present is considerably more than is necessary for the neutralisation of the acid. On the rise of temperature, however, the solution becomes less lævorotatory, and may, when sufficient alkali is present, become quite inactive (T., 1904, **85**, 378).

In the course of work on asymmetric synthesis, one of us had occasion to examine the behaviour of *l*-menthyl *l*-mandelate towards alcoholic potassium hydroxide, and it was found that, no matter under what conditions the saponification was effected, the resulting mandelic acid was invariably racemised to a very considerable extent (T., 1904, **85**, 1249); for example, when a dilute alcoholic solution of the ester was saponified at 25° by the calculated quantity of alkali, the resulting acid had the value $[\alpha]_D$ −36·3° (in aqueous solution), which is less than one-fourth of the value for the pure *l*-acid. For this reason, although unequal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were actually produced by the reduction of *l*-menthyl phenylglyoxylate, the acid obtained by the saponification of this mixture was optically inactive, and this difficulty had to be surmounted before the asymmetric synthesis of *l*-mandelic acid could be successfully accomplished (McKenzie and Humphries, T., 1909, **95**, 1105).

Now mandelic acid, $C_6H_5{\cdot}CH(OH){\cdot}CO_2H$, contains a hydrogen atom and a hydroxyl group, both attached to the asymmetric

carbon atom, and it is conceivable that the phenomena to which reference has been made may have been due to this cause. It was, accordingly, deemed desirable to examine some other acid where the hydroxyl group of mandelic acid had been substituted by a hydrocarbon residue, more especially since data are already available regarding the behaviour of atrolactic acid,

$$OH\cdot CPhMe\cdot CO_2H,$$

where the hydrogen atom of mandelic acid is displaced by a methyl group (T., 1904, **85**, 1249; 1906, **89**, 365). *r*-Phenyl-*p*-tolylacetic acid, $C_7H_7\cdot CHPh\cdot CO_2H$, is readily accessible, and it was accordingly selected for the purpose in view.

The inactive acid was, first of all, resolved. The *d*-acid, which is obtained fairly readily by the agency of cinchonidine, melts at 83—84°, and has $[\alpha]_D$ +14·6° in acetone. Quinine was used for the preparation of the *l*-isomeride, but the resolution was troublesome, as it appeared that the quinine salts of the enantiomorphously related acids formed a solid solution. The *d*-acid undergoes partial racemisation when heated with aqueous alkali, the recovered acid having $[\alpha]_D$ +9·1° in acetone.

The method of Marckwald and McKenzie for resolving inactive compounds, depending on fractional esterification and fractional saponification, was next utilised, and, from the behaviour of the *r*-acid with *l*-menthol, on the one hand, and that of the *l*-menthyl *r*-ester towards alkali on the other, the conclusion was drawn that profound racemisation would take place during the saponification either of the *l*-menthyl *d*-ester or of the *l*-menthyl *l*-ester.

These esters were accordingly prepared separately, and the conclusion was verified. A similar behaviour was exhibited by the *l*-bornyl esters. It was also interesting to note that ethyl *d*-phenyl-*p*-tolylacetate gave an inactive acid on saponification with alcoholic potassium hydroxide. Finally, when the *d*-acid chloride was submitted to the Friedel-Crafts' reaction with benzene and aluminium chloride, the resulting ketone was the racemic form. These experiments showed conclusively that optically active phenyl-*p*-tolylacetic acid is more readily racemised than is mandelic acid under similar conditions.

The hypothesis that racemisation may sometimes be attributed to desmotropic change with the concomitant disappearance of molecular asymmetry is not new. Kipping and Hunter (T., 1903, **83**, 1009) pointed out, with reference to α-benzylpropionic acid, that, from the fact that the asymmetric grouping is in the α-position relatively to the carboxylic group, the change:

$$CH_2Ph\cdot CHMe\cdot CO_2H \longrightarrow CH_2Ph\cdot CMe{:}C(OH)_2$$

would be expected to occur readily; in this case, however, there

was no evidence of racemisation when the acid was heated (compare also Werner, "Lehrbuch der Stereochemie," 1904, 52, 80; Lowry, *British Association Report*, 1904). It would, however, be possible to interpret the racemisation observed by Kipping and Hunter with *d*-benzylpropionyl chloride to the desmotropism of this compound, and we do not doubt that, if the behaviour of the menthyl ester of the *d*-acid were studied, the phenomena exhibited would be similar to those of the menthyl esters of mandelic and phenyl-*p*-tolylacetic acids.

In the same connexion, E. Fischer's well-known observations on the transformation of polyhydroxy-acids of the sugar group by means of pyridine or quinoline are highly significant. In the interconversion, for instance, of *d*-gluconic and *d*-mannonic acids, inversion takes place only at the carbon atom in the α-position, a change which in the light of the above hypothesis would be interpreted as follows:

$$\mathrm{OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}\cdot CO_2H} \rightleftharpoons \mathrm{OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}=\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}} \rightleftharpoons \mathrm{OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}\cdot CO_2H.}$$

Similarly, the establishment of a condition of equilibrium between dextrose, *d*-mannose, and lævulose when any one of these sugars is treated with alkali has been ascribed by Wohl to the formation of a common enolic form.

Within recent years, data in favour of the interpretation of many cases of racemisation on the basis of desmotropism have been gradually accumulating. Incidentally, Aschan's views on the mechanism of the Hell-Volhard reaction (*Annalen*, 1912, **387**, 1; *Ber.*, 1912, **45**, 1913) merit special attention, even although they have not met with general acceptance (compare Lapworth, T., 1904, **85**, 30; Smith and Lewcock, *Ber.*, 1912, **45**, 2358; Meyer, *Ber.*, 1912, **45**, 2868; Michael and Scharf, *Ber.*, 1913, **46**, 136; Staudinger and Anthes, *Ber.*, 1913, **46**, 1417; Aschan, *Ber.*, 1913, **46**, 2162). The bromination of propionyl chloride is represented by this author as follows:

$$\underset{\text{(I.)}}{\mathrm{CH_3\cdot CH_2\cdot COCl}} \longrightarrow \underset{\text{(II.)}}{\mathrm{CH_3\cdot CH{:}CCl\cdot OH}} \xrightarrow{(+Br_2)} \underset{\text{(III.)}}{\mathrm{CH_3\cdot CHBr\cdot CClBr\cdot OH.}}$$

In the hypothetical compound (III) the hydrogen of the hydroxy-group may combine with chlorine or with bromine, so

that a brominated bromide (IV) and a brominated chloride (V) may be produced:

$$\underset{\text{(IV.)}}{CH_3\cdot CHBr\cdot COBr} \xleftarrow{(-HCl)} CH_3\cdot CHBr\cdot CClBr\cdot OH \xrightarrow{(-HBr)} \underset{\text{(V.)}}{CH_3\cdot CHBr\cdot COCl}$$

Since hydrogen has a greater affinity for chlorine than for bromine, the gas evolved should consist mainly of hydrogen chloride, and this has been found experimentally to be the case.

The question of the occurrence of desmotropic change during the racemisation of optically active ketols, such as *l*-benzoin and *d*-benzoylbenzylcarbinol in the presence of alkali, has been considered in former papers (T., 1910, **97**, 473; 1914, **105**, 1583; Wren, T., 1909, **95**, 1583, 1593; compare also Dakin, *Amer. Chem. J.*, 1910, **44**, 48, on the racemisation of hydantoins).

Applying the hypothesis to the case of active mandelic acid, as Lowry (*loc. cit.*) has already done, it will be seen how racemisation might occur:

$$d\text{-}OH\cdot CHPh\cdot CO_2H \longrightarrow OH\cdot CPh{:}C(OH)_2 \longrightarrow r\text{-}OH\cdot CHPh\cdot CO_2H,$$

and similarly with phenyl-*p*-tolylacetic acid and with *iso*propylmalonamic acid (Fischer and Brauns, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 714), which is very easily racemised at the ordinary temperature when an excess of alkali is present.

Now, such a transformation cannot take place with *l*-atrolactic acid, $OH\cdot CPhMe\cdot CO_2H$, as the labile hydrogen atom, which renders possible the formulation of a desmotropic structure, is absent. As has been shown very conclusively (T., 1904, **85**, 1249; 1906, **89**, 365), this acid is remarkably stable towards alkali, and in no case was there ever any evidence of racemisation. Moreover, although the menthyl esters of the *d*- and *l*-atrolactic acids were not prepared separately with the view of testing their behaviour towards alkali, the fact that an optically active acid was invariably obtained by the saponification under various conditions of a mixture of unequal quantities of these esters is a proof that the system is not prone to racemisation. These results have, however, escaped the notice of Rothe, who, in a recent paper (*Ber.*, 1914, **47**, 843), records the stability of active atrolactic acid towards alkali. It may also be observed that the description of the resolution of *r*-atrolactic acid as given by Rothe is imperfect; furthermore, this acid was resolved five years ago (McKenzie and Clough, T., 1910, **87**, 1016), in such a manner as to give the optically pure forms.

The behaviour of *d*-α-amino-α-methylbutyric acid (Fischer and Grävenitz, *Annalen*, 1914, **406**, 1) towards alkali is noteworthy.

As distinct from the commoner α-amino-acids, which are slowly racemised when heated with alkali at 100°, this acid exhibited no racemisation whatever under these conditions. Here, again, the mobile hydrogen atom, necessary for the assumption of desmotropism, is absent. Another instructive example is afforded by the stability towards alkali of the optically active alcohols of the type $CHRR'\cdot OH$; desmotropism is not possible with such compounds, which can be regenerated in an optically pure condition when their esters are treated with alkali (Pickard and Kenyon, T., 1911, **99**, 62, etc.).

Again, Rupe and Häussler (*Annalen*, 1909, **369**, 324) found that *d*-β-phenylbutyric acid, $CHPhMe\cdot CH_2\cdot CO_2H$, could be obtained from its *l*-menthyl ester without the occurrence of racemisation during the process of saponification; similarly, the *l*-menthyl ester of the *l*-acid gave the unracemised acid. Now in the event of desmotropism taking place with these acids, the formation of the compound $CHPhMe\cdot CH{:}C(OH)_2$ does not involve a disappearance of asymmetry, since the original asymmetric carbon atom is still asymmetric according to the latter formulation. The comportment of αβ-diphenylpropionic acid, $CH_2Ph\cdot CHPh\cdot CO_2H$, under similar conditions is, however, different. If this acid, which is isomeric with phenyl-*p*-tolylacetic acid, undergoes transformation into the desmotropic form, $CH_2Ph\cdot CPh{:}C(OH)_2$, a disappearance of asymmetry would result from the change. Now Rupe and Kerkovius (*Ber.*, 1912, **45**, 1398) have found that the optically active αβ-diphenylpropionic acids are completely racemised by alcoholic potassium hydroxide, whilst the acid recovered from the saponification of the *l*-menthyl ester of the *l*-acid is sometimes quite inactive and sometimes only feebly active. This behaviour is, in fact, in the same category with that of mandelic and phenyl-*p*-tolylacetic acids.

Gadamer, who has shown that ethyl *d*-tropate is completely racemised at the ordinary temperature by alcoholic potassium hydroxide, emphasises the contrast between the ester and the free acid, which, so far as his observations go, is not racemised by alkali (*J. pr. Chem.*, 1913, [ii], **87**, 312). On the ground of this difference of behaviour, the assumption is made that the ester behaves as a pseudo-acid, and becomes ionised in the presence of hydroxyl ions:

$$OH\cdot CH_2\cdot \overset{*}{C}HPh\cdot CO_2Et \longrightarrow [OH\cdot CH_2\cdot CPh(CO_2Et)\cdot]' + H^{\cdot}.$$

The disappearance of optical activity is ascribed to the carbon atom C* having only three groups attached to it in the anion, a condition which would involve a symmetrical arrangement owing to three groups falling into one plane with the carbon atom. In the association of the hydrogen ion and the anion by the reverse change,

the *d*- and *l*-esters would be produced in equal quantities. On the other hand, the free acid is assumed by Gadamer to undergo electrolytic dissociation either alone or under the influence of hydroxyl ions into the anion, $(OH\cdot CH_2\cdot CHPh\cdot CO\cdot O\cdot)'$, where the asymmetric carbon atom is still present. However, as Frankland (T., 1913, **103**, 725) has pointed out, the ester might be considered as undergoing isomeric change prior to ionisation, and the disappearance of asymmetry might be attributed to this cause:

$$OH\cdot CH_2\cdot CHPh\cdot CO_2R \longrightarrow OH\cdot CH_2\cdot CPh{:}C(OH)\cdot OR.$$

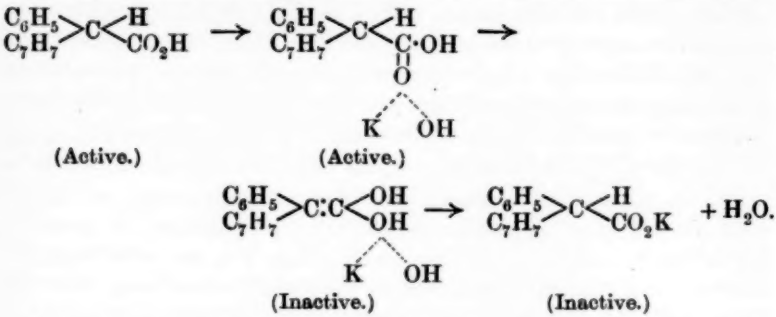
The occurrence of desmotropism appears, therefore, to be the most satisfactory interpretation of the racemisation of optically active compounds by means of alkali which has yet been adduced, and the experimental facts are in remarkable harmony with the idea.

Objection may be raised, however, on very valid grounds to one aspect, which is put forward in the preceding pages. As a convenient working hypothesis, the simplest expression of desmotropism has been employed throughout; the first phase in the process of racemisation by alkali has been represented as an isomeric change; thus, with phenyl-*p*-tolylacetic acid the dihydroxyisomeride has been assumed to be formed in the first instance. Nevertheless, this conception that a complex of the latter type can have even an ephemeral existence in solution appears to us to be extremely improbable. The number of available acids which might undergo such a change is so large that, if the change did actually occur in any case, some definite evidence, either physical or chemical, would undoubtedly be forthcoming. In other words, then, we consider it unlikely that two forms of an optically active acid, such as phenyl-*p*-tolylacetic acid, which can be racemised by alkali, would exist alongside of one another as an equilibrated mixture as represented by $C_7H_7\cdot CHPh\cdot CO_2H \rightleftharpoons C_7H_7\cdot CPh{:}C(OH)_2$, comparable with the tautomerism exhibited by ethyl acetoacetate.

Bearing in mind, however, the reactivity of the carbonyl group,* we suggest that an additive compound is first formed with the catalyst, and that it is this unstable compound, and not the free acid itself, which undergoes desmotropic change. An assumption of this nature does not affect the arguments submitted in favour of the hypothesis of desmotropism during racemisation. The be-

* "Although it has been customary to regard carboxylic acids as compounds containing the free carboxylic radicle, the evidence that such is always the case is in no way sufficient, let alone conclusive. The behaviour of monocarboxylic acids, especially their recognised tendency to form double molecules, as in the case of acetic acid, is clear proof that the carboxylic radicle is far from being saturated" (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, [*A*], **88**, 399).

haviour of active phenyl-*p*-tolylacetic acid towards alkali might, accordingly, be represented by some such scheme as the following, which postulates the addition of the base to the undissociated acid:



Other representations of an equally hypothetical character could, of course, be put forward. We desire, therefore, to emphasise the suggestion that addition precedes desmotropism.

The phenomena of racemisation may be divided broadly into three classes:

(1) Racemisation caused by heating. Werner (*loc. cit.*, pp. 49—50) has discussed this on a kinetic basis.

(2) Catalytic racemisation, by alkali, for example.

(3) Racemisation during reactions involving displacement of groupings.

With reference to this classification it should be observed that various compounds, which are not racemised by alkali, are, nevertheless, convertible by reactions of displacement into compounds which are either quite inactive or are not optically pure; for example, *l*-atrolactic acid gives *r*-α-chloro-α-phenylpropionic acid on treatment with hydrochloric acid (McKenzie and Clough, T., 1910, **97**, 1020); with phosphorus pentachloride, it gives a mixture of *r*- and *d*-α-chloro-α-phenylpropionic acids (McKenzie and Clough, T., 1910, **97**, 2564). Again, *d*-α-amino-α-methylbutyric acid is converted into *r*-α-hydroxy-α-methylbutyric acid by means of nitrous acid (Fischer and Grävenitz, *loc. cit.*). It is possible that the interpretation of catalytic racemisation which has been dealt with in this paper may also be serviceable in connexion with reactions of displacement, such as the Walden inversion.

Experimental.

A modification of the method described by Gyr (*Ber.*, 1908, **41**, 4321) for the preparation of phenyl-*p*-tolylacetic acid was adopted.

One hundred and thirty grams of stannic chloride (1½ mols.) were added gradually to a boiling solution of *r*-mandelic acid (50

grams, 1 mol.) in 250 c.c. of toluene. After two and a-half hours the evolution of hydrogen chloride had practically ceased, and the liquid was then cooled and shaken with an excess of water. The toluene layer was separated, the acid contained in it extracted by sodium carbonate, the alkaline solution filtered, and then acidified by hydrochloric acid. The crude acid, obtained by extraction with ether, was viscous, and became only partly solid by keeping. It was crystallised from dilute acetic acid, from which solvent, as well as from others, it separated as an oil, which, however, readily solidified on being sown with a nucleus. The melting point was 115—116°, whereas Zincke (*Ber.*, 1877, **10**, 997) gives 115°. The yield was 32 grams.

Resolution of r-*Phenyl*-p-*tolylacetic Acid.*

Cinchonidine was found to be a suitable alkaloid for this purpose. When 6·5 grams of the alkaloid (1 mol.) were dissolved in a solution of 5 grams of the acid (1 mol.) in 160 c.c. of ethyl alcohol, 8·5 grams of crystals separated; these were crystallised twice from ethyl alcohol, and the resulting 4 grams gave 1·5 grams of acid with $[\alpha]_D + 10°$ in acetone. On the other hand, when 5 grams of the *r*-acid were dissolved in 90 c.c. of alcohol and combined with 3·25 grams of the alkaloid ($\frac{1}{2}$ mol.), the crystals, which separated, amounted to 4 grams, and gave 1·7 grams of acid with $[\alpha]_D + 7·9°$ in acetone. It was, therefore, advantageous to employ the acid and the alkaloid in molecular quantities.

Fifty grams of the *r*-acid (1 mol.) were dissolved in 2 litres of boiling ethyl alcohol, and 65 grams of cinchonidine (1 mol.) were added. Crystallisation proceeded during two days in an ice-chest. The 54 grams of salt which separated were crystallised as before from 900 c.c. of alcohol, and, after five additional crystallisations, the salt (24 grams), which separated in needles, was homogeneous. It melted and decomposed at 204—205°, and, after being dried at the ordinary temperature, it gave the following values when dissolved in chloroform; $l = 2$, $c = 3·025$, $\alpha_D^{16} - 2·12°$, $[\alpha]_D^{16} - 35°$. It was decomposed by shaking with an excess of dilute sulphuric acid, and the organic acid was then extracted with ether. Yield of acid, 9·2 grams.

d-*Phenyl*-p-*tolylacetic acid*, $C_7H_7·CHPh·CO_2H$, separates from aqueous alcohol or from dilute acetic acid as an oil, which solidifies gradually to form feathery needles. It is very soluble in ethyl alcohol, acetone, benzene, chloroform, and acetic acid. It melts at 83—84° with slight preliminary softening. For analysis, it was dried in a vacuum over sulphuric acid:

0·175 gave 0·5096 CO_2 and 0·0982 H_2O. C = 79·4; H = 6·2.
$C_{15}H_{14}O_2$ requires C = 79·6; H = 6·2 per cent.

Its specific rotation was determined in acetone:

$l = 2$, $c = 4·214$, $\alpha_D^{19·4} + 1·23°$, $[\alpha]_D^{19·4} + 14·6°$.

Owing to the small rotatory power of the acid both in acetone and in other solvents, polarimetric measurements of the cinchonidine salts obtained from each separate crystallisation are of little value as an indication of the progress of the resolution. In order to establish the purity of the acid as prepared by the method just described, the filtrate from each crop in another resolution was decomposed by mineral acid, and the resulting organic acid examined. Thirty-nine grams of cinchonidine were dissolved in a solution of 30 grams of the *r*-acid in 1200 c.c. of ethyl alcohol, the progress of the separation being shown as follows:

	Cinchonidine salt.	Alcohol.	Acid from filtrate.	$[\alpha]_D^r$ in Acetone.*
1	36 grams	600 c.c.	14·0 grams	−4·3°
2	29 ,,	500		
3	23 ,,	380	1·3 ,,	+1·6
4	21 ,,	345	0·8 ,,	7·1
5	18 ,,	300	0·6 ,,	9·9
6	16 ,,	250	0·5 ,,	11·7
7	14 ,,	230	0·5 ,,	14·6
8	12·5 ,,	225	0·3 ,,	not examined.
9	11·0 ,,	210	0·3 ,,	14·4
10	10·5 ,,	190	0·3 ,,	14·2
11	9·0 ,,	170	0·4 ,,	14·6
12	7·0 ,,	(gave an acid with $[\alpha]_D + 14·5°$).		

* The influence of temperature on the rotatory power between 12° and 33° was found to be very slight.

A portion of the acid with $[\alpha]_D + 14·5°$ was converted into the calcium salt, from the aqueous solution of which two separate fractions of crystals were withdrawn; the acids obtained from these fractions gave in each case the value $[\alpha]_D + 14·4°$.

Since the pure acid does not have a sharp melting point, tends to separate as an oil from aqueous alcohol, and does not crystallise readily from other solvents, some such proof of its homogeneity as that just given was rendered necessary. It may also be added that the separation of the pure *d*-acid by crystallising a mixture of it and the *r*-acid from aqueous alcohol is not practical, even when the proportion of the *r*-acid present is small.

For the preparation of the *l*-acid, the various amounts of the lævorotatory acid mixture, obtained from the mother liquors of the first crystallisations during the isolation of the *d*-acid by cinchonidine, were united, dissolved in alcohol, and combined with quinine. The separation of the pure quinine *l*-salt is not, however, accomplished readily. Thus 34·8 grams of the lævorotatory acid

mixture were dissolved in 170 c.c. of ethyl alcohol and combined with 24·7 grams of quinine. Fine needles (35 grams) separated on cooling, and a portion on decomposition with mineral acid gave an acid with $[\alpha]_D$ −8·3° in acetone. Nevertheless, even after ten crystallisations the pure quinine *l*-salt was not obtained, since the acid resulting from the crystals (10 grams) had only $[\alpha]_D$ −11·5°, a value which is about 3° too low. A better result was obtained in another experiment, where 121 grams of a lævorotatory acid mixture were combined with 86 grams of quinine. After seven crystallisations from alcohol, the salt amounted to 47 grams, whilst the acid obtained from it had $[\alpha]_D$ −13·9° in acetone, and was therefore almost pure.

The difficulty in preparing the *l*-acid is to be attributed in all probability to the formation of mixed crystals of the quinine salts of the enantiomorphously related acids. The separation of such a product must necessarily be tedious; compare, for example, Schütz and Marckwald (*Ber.*, 1896, **29**, 52) on the resolution of *dl*-valeric acid, and Perkin, Pope, and Wallach (T., 1909, **95**, 1789) on the resolution of 1-methyl*cyclo*hexylidene-4-acetic acid.

Action of Aqueous Potassium Hydroxide on the d-*Acid.*

1·7238 Grams of *d*-phenyl-*p*-tolylacetic acid were heated at 100° for one hour with 34 c.c. of aqueous potassium hydroxide, the amount of alkali present being twice that necessary for neutralisation. The acid was then recovered, and was found to have undergone partial racemisation; it melted indefinitely, and gave the following value in acetone:

$$l=2,\ c=5·591,\ \alpha_D +1·02°,\ [\alpha]_D +9·1°.$$

Activation of the r-*Acid by Fractional Esterification.*

Five grams of the *r*-acid (1 mol.) were heated with 3·45 grams of *l*-menthol (1 mol.) for three hours at 150°. The product was manipulated as described by Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130) in connexion with the esterification of mandelic acid with menthol. 3·4 Grams of unesterified acid were recovered, and this was slightly dextrorotatory, a solution of 1·75 grams made up to 10 c.c. with acetone giving α_D +0·11° in a 2-dcm. tube. Very little esterification had, however, taken place, since only 0·25 gram of acid (inactive) was recovered by saponifying the esters formed.

A more decided effect was attained by esterifying 10 grams of the *r*-acid with an excess of menthol (30 grams) in the presence of 3 grams of sulphuric acid, the mixture being heated at 100° for four hours. The unesterified acid amounted in this case to

2·1 grams; 0·64 gram of it, when made up to 25 c.c. with acetone, gave α_D +0·19° in a 4-dcm. tube. It appeared, therefore, that *l*-phenyl-*p*-tolylacetic acid is esterified by *l*-menthol slightly more quickly than is the *d*-isomeride. The ester mixture, obtained after the removal of the unesterified acid and the excess of menthol, amounted to about 8 grams, and consisted of *l*-menthyl *d*-ester and *l*-menthyl *l*-ester, the latter being slightly in excess. The saponification was conducted by dissolving the oil in 180 c.c. of alcoholic potassium hydroxide containing twice the calculated amount of alkali, and allowing to remain at the ordinary temperature for one and a-half days. 3·5 Grams of acid were recovered, and it was optically inactive. Accordingly, since the mixture of esters mentioned above did not, when saponified, give a lævorotatory acid, complete racemisation had taken place during the process of saponification. The individual esters were subsequently prepared, and their behaviour towards alkali examined.

Action of Alkali on the Menthyl Esters.

By means of thionyl chloride, *r*-phenyl-*p*-tolylacetic acid was converted into its acid chloride, which was then acted on by menthol in the presence of benzene and pyridine. Yield of ester, 75 per cent.

l-*Menthyl* r-*phenyl*-p-*tolylacetate* boils at 250°/12 mm. It was blue when freshly distilled, but the colour disappeared gradually. The oil solidifies slowly. The solid ester melts at 54—55°, and separates from aqueous alcohol in rectangular crystals. Its rotatory power was unaltered when it was crystallised from aqueous alcohol. Apparently it was partially racemic, and did not undergo resolution into its diastereoisomerides under the temperature conditions employed in its crystallisation from aqueous alcohol:

0·2921 gave 0·8836 CO_2 and 0·2296 H_2O. C=82·5; H=8·8.

$C_{25}H_{32}O_2$ requires C=82·4; H=8·9 per cent.

The determination of the specific rotation was made in acetone: $l=2$, $c=5·625$, $\alpha_D^{15·6}$ −6·66°, $[\alpha]_D^{15·6}$ −59·2°. On submitting 12 grams of this ester to fractional saponification, three different fractions of acid were obtained, and these were all feebly lævorotatory.

l-*Menthyl* d-*phenyl*-p-*tolylacetate*, prepared from *d*-phenyl-*p*-tolylacetyl chloride, separates from aqueous alcohol in feathery needles and melts at 53—54°:

0·1988 gave 0·6000 CO_2 and 0·1530 H_2O. C=82·3; H=8·6.

$C_{25}H_{32}O_2$ requires C=82·4; H=8·9 per cent.

In acetone solution:

$l=2$, $c=5·746$, α_D^{14} −6·09°, $[\alpha]_D^{14}$ −53·0°.

Four grams of this ester were boiled for one hour and twenty minutes with 100 c.c. of alcoholic potassium hydroxide containing slightly more than the quantity of alkali required for complete saponification. The alcohol was distilled off, and the residue submitted to distillation in steam in order to separate the free menthol, and then extracted with ether to remove unsaponified ester. The acid (0·8 gram), isolated from the potassium salt, exhibited no optical activity. Bearing in mind the slowness with which the esterification of the *r*-acid by direct heating with menthol occurred, it was not surprising that the saponification of the ester was also a slow process, and was, on this account, incomplete when conducted under the conditions quoted; in fact, no less than 2·2 grams of unsaponified ester were recovered. The value for the rotatory power of this latter product was $[\alpha]_D$ −54·7° in acetone, a result perhaps not devoid of significance, indicating as it does that the ester is in part catalytically racemised by alkali prior to its undergoing saponification. This unsaponified ester was next boiled for one and a-half hours with 100 c.c. of alcoholic potassium hydroxide containing slightly more alkali than the amount requisite for complete saponification. The acid (0·3 gram) obtained from the potassium salt was practically inactive; when made up to 10 c.c. with acetone it gave α_D +0·06° in a 2-dcm. tube. The residual ester (1·2 grams) was heated as before with alcoholic potassium hydroxide, and the resulting acid was inactive.

l-*Menthyl* l-*phenyl*-p-*tolylacetate*, prepared from *l*-phenyl-*p*-tolylacetyl chloride, melts at 57—58°. It was crystallised from aqueous alcohol:

0·1863 gave 0·5615 CO_2 and 0·1441 H_2O. C = 82·2; H = 8·7.
$C_{25}H_{32}O_2$ requires C = 82·4; H = 8·9 per cent.

The *r*-acid was obtained by the saponification of this ester.

Action of Alkali on the Bornyl Esters.

l-*Bornyl* dl-*phenyl*-p-*tolylacetate*, prepared by the action of *l*-borneol on *dl*-phenyl-*p*-tolylacetyl chloride in the presence of benzene and pyridine, is an oil which boils at 249°/12 mm. When freshly distilled, it had a bright blue colour:

0·2460 gave 0·7456 CO_2 and 0·1814 H_2O. C = 82·7; H = 8·3.
$C_{25}H_{30}O_2$ requires C = 82·8; H = 8·3 per cent.

This ester was submitted to fractional saponification, and the specimens of acid obtained were optically inactive.

l-*Bornyl* d-*phenyl*-p-*tolylacetate* is an oil, which boils at 240°/13 mm.:

0·2394 gave 0·7270 CO_2 and 0·1764 H_2O. C = 82·8; H = 8·2.
$C_{25}H_{30}O_2$ requires C = 82·8; H = 8·3 per cent.

3·6 Grams of this ester were heated for one and a-quarter hours with 100 c.c. of alcoholic potassium hydroxide containing slightly more than the calculated quantity of alkali. 0·5 Gram of ester escaped saponification, whilst the recovered acid was optically inactive. When the saponification was conducted at the ordinary temperature during seven days, the recovered acid was only slightly dextrorotatory, having $[\alpha]_D$ + 0·9° in acetone.

Action of Alkali on the Ethyl d-*Ester.*

Ethyl d-*phenyl*-p-*tolylacetate*, prepared by esterifying the *d*-acid with ethyl alcohol and hydrogen chloride, separates from aqueous alcohol in feathery needles, and melts at 39—40°, whereas the inactive isomeride melts at 34° (Zincke, *loc. cit.*). It dissolves readily in the commoner organic solvents:

0·1900 gave 0·5590 CO_2 and 0·1256 H_2O. C = 80·2; H = 7·4.
$C_{17}H_{18}O_2$ requires C = 80·3; H = 7·1 per cent.

In acetone solution:

$l = 2$, $c = 8·231$, α_D^{15} + 1·71°, $[\alpha]_D^{15}$ + 10·4°.

2·5 Grams were heated for one hour with 50 c.c. of alcoholic potassium hydroxide, containing alkali in an amount just exceeding that necessary for complete saponification. The acid recovered was optically inactive when examined in acetone solution.

Conversion of the d-*Acid into* r-*Phenyl*-p-*tolylacetophenone.*

Ten grams of *r*-phenyl-*p*-tolylacetic acid were converted into the acid chloride by means of thionyl chloride. A solution of this acid chloride in carbon disulphide was added gradually to a mixture of 9 grams of aluminium chloride, 44 grams of benzene, and 18 grams of carbon disulphide, the action being conducted under diminished pressure for about one hour. After two days at the ordinary temperature, water and then dilute hydrochloric acid were added, and the benzene and carbon disulphide removed by steam. The residue was extracted with ether. When the ethereal solution was allowed to evaporate spontaneously, 1·4 grams of solid separated from an oil, and, on crystallising this from a mixture of benzene and light petroleum, 1 gram was obtained.

r-*Phenyl*-p-*tolylacetophenone*, C_7H_7·CHPh·COPh, separates from a mixture of benzene and light petroleum in hexagonal plates, and melts at 159—160°:

0·1258 gave 0·4058 CO_2 and 0·0696 H_2O. C = 88·0; H = 6·2.
$C_{21}H_{18}O$ requires C = 88·1; H = 6·3 per cent.

On distilling the oil from which this solid had been withdrawn, a fraction was obtained which boiled at 120°/15 mm.; it separates from aqueous alcohol in transparent crystals, and melts at 28—29°.

Ten grams of the *d*-acid were submitted to the Friedel and Crafts' reaction, the conditions being similar to those just described. 1·4 Grams of crude ketone were obtained. This amount was crystallised from a mixture of benzene and light petroleum. The product was the racemic ketone, no optical activity being observed with its ethyl-alcoholic solution.

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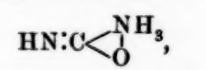
[*Received, April 8th*, 1915.]

LXXVI.—*The Constitution of Carbamides. Part II. The Relation of Cyanamide to Urea. The Constitution of Cyanamide and the Mechanism of its Polymerisation.*

By EMIL ALPHONSE WERNER.

THE constitution of cyanamide and its hydrolysis to urea have a special interest in connexion with the cyclic formula for the latter substance which has been proposed by the author (T., 1913, **103**, 1014, 2281). It was recently shown (T., 1914, **105**, 924) that urea assumes the "*iso*-carbamide" configuration in its reaction with methyl sulphate, this being derived from the structure:



which it is contended represents the true constitution of urea in the static condition, and when dissolved in a neutral solvent.

Whilst the main object of the present investigation was to obtain information regarding the structural relations of urea and cyanamide, the polymerisation of the latter has been incidentally examined, since this is a phenomenon which must be intimately associated with its constitution. A theory which explains the mechanism of the change, in complete agreement with all the observed facts, is now put forward, and is dealt with first, since it has a very important bearing on the main question under consideration.

The Polymerisation of Cyanamide.

Two papers on this subject have appeared recently, one by Grube and Krüger (*Zeitsch. physikal. Chem.*, 1913, **86**, 65), and the other by Morrell and Burgen (T., 1914, **105**, 576). Both investigations have shown that the well-known polymerisation of cyanamide to dicyanodiamide is greatly accelerated by the presence of alkalis, even in small amount, whilst Morrell and Burgen have also shown that an equally powerful accelerating effect is produced by acids.

The most interesting results which the latter investigators have brought to light are those dealing with the behaviour of cyanamide in the absence of either acid or base. They have shown that in a neutral aqueous solution cyanamide is remarkably resistant to polymerisation, a fact which is even more evident in the presence of alcohol, and, indeed, their results go to show that under such conditions cyanamide probably does not suffer polymerisation at all. Whilst the experimental results recorded in both investigations are beyond question, their interpretation and the conclusions drawn from them are certainly open to criticism.

An attempt has been made in both cases to explain the phenomenon of polymerisation by the aid of a purely ionic theory, which, as Morrell and Burgen freely admit, is not in harmony with all the observed facts, since they state that "a single explanation which will cover the accelerating action of both acids and bases cannot be put forward." Grube and Krüger (*loc. cit.*), who have only examined the influence of bases on the change, are satisfied with an ionic theory, and conclude that the course of the polymerisation proceeds according to the scheme:

$$\underset{\text{Cyanamidion.}}{CN\cdot NH_2} + \underset{\text{Cyanamidion.}}{CN\cdot NH'} = \underset{\text{Dicyanodiamidion.}}{C_2N_2N_2H_3'},$$

an explanation which certainly throws very little light on either the cause or the mechanism of the change.

It must be remembered that cyanamide undergoes polymerisation when heated alone, in the absence of any solvent, and also when heated (at 150°) in solution in a non-ionising solvent, such as dry ether, as was shown long since by Drechsel (*J. pr. Chem.*, 1877, [ii], **9**, 284), and since there is no reason to conclude that the mechanism of the polymerisation under these conditions is different from that under the conditions just mentioned, it is obvious that an ionic theory which cannot include all the facts cannot be sound.

Curiously enough, in neither of the investigations has the primary question of the constitution of cyanamide itself been dis-

cussed; the structural formula, $CN\cdot NH_2$, has alone been considered to represent all the properties of the substance, a conclusion which has certainly helped greatly to obscure the meaning of the observed facts.

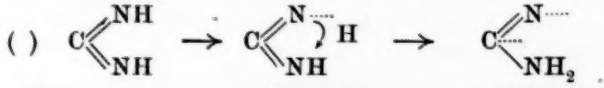
Now it must be conceded that the properties of cyanamide are in every sense characteristic of a tautomeric substance, and the constitution of the compound may be equally well expressed by the di-imino formula $C(NH)_2$; in the author's opinion both configurations of the molecule are present in a pure neutral solution, and the remarkable stability of cyanamide under such condition,* as shown by the experimental results of Morrell and Burgen, is very probably due to an electrostatic equilibrium between the two forms, which may be represented by the scheme:

$$(a).\ NH{:}C{:}NH. \rightleftharpoons CN\cdot NH_2\ (b).$$

Acidic form (−). Basic form (+).

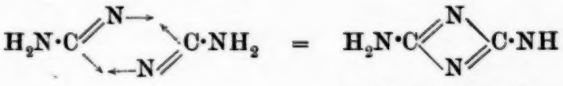
If this view be taken, the mechanism of the polymerisation may be easily explained by the aid of a theory similar to that put forward by the author to explain the polymerisation of the related cyanic acid (T., 1913, **103**, 1017), which will be found to cover all the observed facts.

Thus the addition of either an acid or a base to a neutral solution of cyanamide will disturb the above equilibrium, and polymerisation will soon commence as the result of an effort to maintain the equilibrium; for example, if a sufficiently strong acid be added to the solution it will at once exert a neutralising effect on the electropositive form (*b*), and will cause form (*a*) to change into form (*b*) in order to meet the new condition; polymerisation will then take effect, as illustrated in the following scheme:



(−.) (Phase 1) (Phase 2.)

the union of two molecules in phase (2) will give rise to the formation of dicyanodiamide, thus:

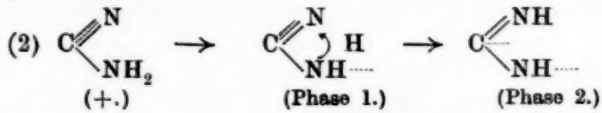


Hofmann's formula.

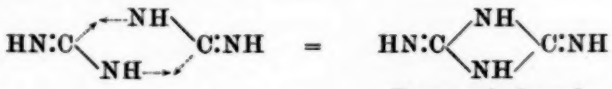
On the other hand, if a base be added to the solution it will

* The author has had in his possession an aqueous solution of pure cyanamide for more than four and a-half years, at the end of which time it still contained a large proportion of the unchanged substance.

neutralise the electronegative form (*a*), and (*b*) will then change in the following order:



and the union of two molecules in phase (2) will give rise to the formation of dicyanodiamide, thus:



Baumann's formula.

Dicyanodiamide, like cyanamide, is also a tautomeric substance, but, unlike cyanamide, is not capable of yielding salts with either acids or bases, and is, as Caro and Grossmann have shown (*Chem. Zeit.*, 1909, **33**, 734), a perfectly neutral substance; it can therefore be only a transition product formed from the cyanamide in its efforts to attain equilibrium (neutrality) with the base or acid present. In the latter case equilibrium is quickly reached by the hydrolysis of the dicyanodiamide to the strong base, the so-called dicyanodiamidine. As a matter of fact, the latter change appears to proceed with at least as great a velocity as the polymerisation of the cyanamide, since dicyanodiamidine can be detected in the solution as soon as the cyanamide commences to disappear. For this reason it has not been found possible to isolate any dicyandiamide from the product of the action of an acid on a solution of cyanamide.

In the case of the action of bases, dicyanodiamide can be easily obtained, this being the method commonly employed for its preparation; nevertheless, this does not represent final equilibrium under the conditions.

Dicyanodiamide is sensitive to hydrolysis by alkalis, a fairly strong acid, probably Hallwachs' amidodicyanic acid, being formed (ammonia and carbon dioxide being by-products), which ultimately neutralises the alkali. Whilst the velocity of this change is undoubtedly very much slower than the velocity of polymerisation of cyanamide in the presence of alkali, still its influence cannot be ignored, particularly in experiments where the heating at 100° was prolonged.

Morrell and Burgen have scarcely given this question the attention it deserves; it probably helps to explain the gradual decrease in the velocity of polymerisation which they observed. Their contention that during the course of the reaction the base (sodium hydroxide) is shared by the dicyanodiamide, and that this is dis-

sociated primarily as a monobasic acid, is scarcely in agreement with the properties of the substance.

Whilst cyanamide affords a neutral solution, its acid character in so far as the production of metallic derivatives is concerned, is well known, and is very much more pronounced than the basic power; thus, according to Grube and Krüger, the salt NaN:C:NH in a molecular solution is dissociated only to the extent of about 3 per cent.

It seems evident, therefore, that a weak base should have a much greater disturbing effect on the equilibrium between the two forms of cyanamide than a correspondingly weak acid, and hence cause a much greater acceleration of the polymerisation.

In order to test this point, the behaviour of cyanamide in the presence of acetic acid has been examined; the results are given below, and for comparison a few values, calculated from Morrell and Burgen's experiments in the presence of ammonia, have been added.

The concentration of cyanamide was approximately 2 per cent.

(*a*) Cyanamide heated in a water-bath at 100° for two hours:

	Per cent. of cyanamide polymerised.
In *N*/20-Acetic acid	6·3
„ *N*/10 „ „	8·8
„ *N*/4 „ „	16·3
„ *N*/2 „ „	21·9

(*b*) Cyanamide, heated as above in *N*/2-acetic acid, was polymerised as follows:

1. 3 hours, 28·8. 2. 4 hours, 33·8. 3. 5 hours, 38·1 per cent.

(*c*) Cyanamide heated in the presence of normal acetic acid for ten hours was polymerised to the extent of 63·5 per cent.

(*d*) Cyanamide heated as above in the presence of ammonia (M. and B.):

In *N*/70-Ammonia.		In *N*/7-Ammonia.	
Time.	Cyanamide polymerised.	Time	Cyanamide polymerised.
2·5 hours	28·0 per cent.	1 hour	80·1 per cent.
4·5 „	39·5 „	1·5 hours	92·4 „
8·5 „	52·0 „	3 „	100·0 „

It will be noticed that in order to obtain well-marked results with acetic acid it was necessary to start with a concentration of not less than *N*/20, and an inspection of the values obtained shows at once the enormously greater accelerating power of the weak base.

Thus the amount of polymerisation produced by *N*/2-acetic acid is only equal to that produced by *N*/70-ammonia under approxi-

mately the same conditions, whilst after five hours the effect of $N/2$-acetic acid is less than half that produced by $N/7$-ammonia in one hour. These results are quite in agreement with the equilibrium theory, bearing in mind the properties of cyanamide.

The accelerating effect of even a trace of alkali on the polymerisation was so great, as shown by the very careful experiments of Morrell and Burgen, that one might easily have arrived at the erroneous conclusion that cyanamide was more stable in the presence of acetic acid than in aqueous solution.

For example, the following results were obtained (*e*) after heating a solution of cyanamide (3 per cent. approximately) in ordinary distilled water at 100° in a soft glass tube, (*f*) after keeping the solution at the ordinary temperature:

(*e*) Time in hours.	Cyanamide polymerised	(*f*) Time.	Cyanamide polymerised.
2	27·5 per cent.	After 10 weeks	29·4 per cent.
4	33·2 ,,	,, 12 ,,	37·5 ,,
9	56·8 ,,	,, 11 months	81·8 ,,
16	86·5 ,,		

These results, which are higher than those obtained by Morrell and Burgen, are entirely due to basic matter extracted from the glass, and they serve merely to illustrate how the acceleration of the change may vary according to the quality of the glass vessel employed.

In the experiments where a solution of cyanamide was heated at 100° for nine and sixteen hours respectively, a small quantity of a basic substance separated in each case; this proved to be neither melamine nor ammeline, and has not yet been identified.

The polymerisation of cyanamide by heat alone, which is the chief factor in promoting the change, all other conditions being equal, can also be explained by the theory just described.

An increase in the vibratory motion within the molecule will naturally accompany a rise in temperature, and the stability of the cyanamide molecule will be thereby diminished, and the less stable form will tend to change into the more stable in accordance with one or other of the two schemes already given.

The direction of the change must depend on this relative stability of the two forms, and since the balance of evidence certainly favours the greater stability of the di-imino- or symmetrical form, the change will very probably take the course indicated in scheme (2).

The more complex polymerisation of cyanamide at high temperatures (above 200°) with the production of the very strong base melamine is also in agreement with this view.

The sudden depolymerisation of dicyanodiamide by heat will

give rise for the moment to cyanamide in the di-imino-form, the tendency to co-exist in equilibrium with the amino-form will persist, and by the union of three molecules in phase (2),

$$H_2N\cdot C\langle^{N-}_{\text{---}},$$

scheme (1), the very stable, six-membered ring melamine,

$$NH_2\cdot C\langle^{N\cdot C(NH_2)}_{N:C(NH_2)}\rangle N,$$

will be formed.

It may be added, in further support of the scheme (1), that a small quantity of melamine has always been detected in the product from the polymerisation of cyanamide in the presence of acids, but could not be found when bases were used.

The presence of traces of melamine and dicyanodiamidine in solutions containing an excess of cyanamide or dicyanodiamide may be easily recognised by the aid of picric acid.

Melamine picrate forms characteristic, tangled masses of extremely delicate, hair-like threads of a pale yellow colour, which decompose, without melting, at about 268°; dicyanodiamidine picrate separates slowly from solution in the form of nodules, or small rosettes of stout prisms of a dark yellow colour, which melt at 265°.

Interaction of Cyanamide and Nitrous Acid.

The behaviour of cyanamide towards nitrous acid does not appear to have been hitherto examined. A few quantitative experiments have supplied what appears to be conclusive evidence in favour of the views already expressed regarding the constitution of cyanamide in solution.

The experiments were carried out in a nitrometer, and the details are described in the experimental part of the paper.

The main facts observed may be stated as follows:

(1) Cyanamide and nitrous acid (liberated from sodium nitrite by an excess of acetic acid) showed practically no signs of interaction, so far as the evolution of gas was concerned, even after one hour.

Such a negative result could scarcely have been expected if cyanamide was wholly present in the form $CN\cdot NH_2$.

(2) In the presence of sulphuric acid there was an immediate brisk evolution of gas (almost entirely nitrogen), which, after an interval of two minutes, amounted to half the theoretical volume required by the equation:

$$CN\cdot NH_2 + ON\cdot OH = N_2 + H_2O + CN\cdot OH.$$

This was followed by a very slow and continuous evolution of gas

largely composed of carbon dioxide, and therefore mainly due to the gradual hydrolysis of the cyanic acid generated in the first stage. An interval of one hour was required for the evolution of a volume of gas equal to that set free in the first few minutes. An examination of the residual liquid at this point showed that slightly over half of the cyanamide was still unchanged, whilst there was much nitrous acid present (see Expt. I).

(3) When the reaction was allowed to proceed for twenty minutes, nearly 60 per cent. of the cyanamide was unchanged, and in a final experiment, where the reaction was allowed to continue for twenty hours, nearly 13 per cent. of the cyanamide was still undecomposed (see Expts. II and III).

In spite of the secondary change introduced by the continuous decomposition of cyanic acid, the results have shown that the course of the reaction is in perfect harmony with the equilibrium theory; thus whilst all the cyanamide present at the outset in the amino-form is rapidly decomposed by nitrous acid in the usual manner, the more stable imino-form at the ordinary temperature changes very slowly into the amino-form, which is then attacked by nitrous acid as fast as it is generated. The results also indicate that in a normal solution of cyanamide the equilibrium mixture is approximately 60 per cent. $C(NH)_2$ and 40 per cent. $CN{\cdot}NH_2$ (Expt. II).

The Formation of Urea by the Hydrolysis of Cyanamide.

A study of the constitution of cyanamide was a necessary preliminary to an examination into the mechanism of its hydrolysis. The formation of urea from cyanamide was originally shown many years ago by Baumann (*Ber.*, 1873, **6**, 1373), but the exact conditions under which the hydrolytic change takes place have not, in the author's opinion, been properly appreciated. Thus Baumann showed that whilst very concentrated acid was necessary to obtain urea (as a salt) from cyanamide, this was always accompanied by more or less dicyanodiamidine, the proportion of the latter increasing with the dilution of the acid, and Drechsel (*J. pr. Chem.*, 1880, [ii], **20**, 77) has pointed out that the compound

$$CN{\cdot}NH_2,2HCl,$$

when decomposed by water, did not afford urea, but only dicyanodiamidine.

The usual equation, $CN{\cdot}NH_2 + H_2O = H_2N{\cdot}CO{\cdot}NH_2$, so freely expressed in text-books and works of reference, and commonly accompanied by the simple statement that cyanamide readily combines with water to form "carbamide," besides being mislead-

ing when the real facts are considered, has led to the impression that cyanamide is a substance easily hydrolysed. This is not the case.

Whilst cyanamide is readily polymerised when heated in the presence of dilute acids or alkalis, it is remarkably resistant to hydrolysis, as is shown by the fact that not a trace of urea can be detected in the products after heating solutions of cyanamide for various intervals of time under the aforesaid conditions.

Negative results, so far as the hydrolysis to urea was concerned, were also obtained after heating cyanamide with water alone for several hours at 100°, and after heating in a sealed tube at 120—130° for three hours.

A comparison of the urea formula, $HN{:}C\begin{matrix}NH_2\\O\end{matrix}$, with either of the two formulæ of cyanamide shows that the relation between the two compounds is evidently not the simple one so generally supposed, namely, that of nitrile and amide.

By the addition of nitric acid (D 1·42) to a solution of cyanamide in moist ether, Baumann (*loc. cit.*) obtained urea nitrate together with more or less of the nitrate of dicyanodiamidine, but the production of urea in the free state directly from cyanamide by hydrolysis has not yet been accomplished.

A quantitative study of Baumann's experiment has shown that whilst the proportion of water present may be more than sufficient to hydrolyse all the cyanamide in solution, the amount of urea nitrate formed is determined by the quantity of nitric acid added. When the latter was insufficient in amount to form urea nitrate from all the cyanamide present, the excess of this remained unchanged; it was not polymerised, since the nitric acid was removed from solution by the urea generated, and the equilibrium of the remaining cyanamide was not further disturbed (see Expts. IV and V). When, on the other hand, the amount of water present was sufficient (without being in very great excess) to bring about the complete dissociation of the salt of urea, if formed, then no urea was generated, and the cyanamide was slowly polymerised with the subsequent production of dicyanodiamidine.

These results, which are in marked contrast to those commonly associated with the hydrolysis of nitriles or amides, may be readily explained if the mechanism of the change be carefully considered, and supply, in the author's opinion, an interesting confirmation of his views regarding the constitution of urea in the static condition and in the presence of an acid.

The conditions show that cyanamide must have assumed the

amino-form before hydrolysis, and since the ions $H^{\cdot}$ and OH' are undoubtedly the active agents which take part in the change, this may be represented by the following equation:

$$C\begin{matrix}\diagup NH_2 \\ \equiv N\end{matrix} + H^{\cdot} + OH' + HNO_3 = C\begin{matrix}\diagup NH_2\cdot HNO_3 \\ = NH \\ \diagdown OH\end{matrix}.$$

This reaction, which is analogous to the formation of *iso*carbamides from cyanamide and alcohols in the presence of hydrogen chloride, shows that urea, when generated, has the *iso*carbamide configuration, which is retained only in the salt and in the presence of a small quantity of water.

Now the hydrolysis of cyanamide is a rapid change which proceeds at the ordinary temperature, in contrast to polymerisation, which is a very slow change unless aided by heat; therefore, the formation of urea nitrate must be the outcome of a rapid effort to attain more stable equilibrium under the disturbing influence of the strong acid. This stability can only be attained provided the conditions are such that a salt of urea can be formed, because the *iso*carbamide configuration of the urea molecule is too unstable to exist in the static condition, and hence urea can only be generated in quantity sufficient to form a salt with the particular amount of acid present. It follows, therefore, that if the salt cannot exist even though acid be present, a condition brought about, for example, by the presence of too much water, no urea can be formed, which, as the experiments have shown, was actually the case. In further confirmation of this, it may be mentioned that fuming hydrochloric acid was added to cyanamide dissolved in moist ether, and after keeping for twenty-four hours, practically all the cyanamide was found unchanged (Expt. VI).

Apart even from the remote relationship between cyanamide and urea, as indicated by the cyclic structure of the latter, the fact that cyanamide has not been, and probably cannot be, directly hydrolysed to yield urea in the free state, is in perfect agreement with the above explanation of the mechanism of the change.

Thus whilst it is true that urea in its static condition is a more stable compound than cyanamide, it is equally true that the latter must be much more stable than urea when this is in its tautomeric or *iso*carbamide configuration, and hence the more stable compound cannot be produced through the intermediary of a substance less stable than cyanamide itself.

In conclusion, it may be added that if cyanamide is related to urea, as nitrile to amide, and if urea has the "carbamide" structure both in the free state and as a salt, as is generally supposed, the facts observed become unintelligible, and there appears no

reason why cyanamide should not be hydrolysed in the normal manner, and be capable of directly furnishing urea whether a certain fixed quantity of acid were present or not.

The converse change, namely, the production of cyanamide from urea, will form the subject of another communication. It may be stated here that the facts hitherto recorded regarding the formation of cyanamide by the removal of the elements of water from urea, have not been confirmed.

Experimental.

Polymerisation of Cyanamide in the Presence of Acetic Acid.

The estimations of cyanamide were made by precipitation with an excess of $N/10$-ammonio-silver nitrate solution, the excess of silver being estimated by Volhard's method. The details and precautions recommended by Morrell and Burgen were carefully adhered to, and in some cases the estimations were checked by a direct weighing of the precipitated silver cyanamide previously dried at 100°.

In view of the work already published by the above-mentioned investigators, the following few results will suffice to illustrate how the values already given were obtained.

Five c.c. of the cyanamide solution used required 53·3 c.c. $N/10$-$AgNO_3$ (1 c.c. = 0·0021 gram CN_2H_2); the concentration of cyanamide was therefore 2·24 per cent. After heating for two hours at 100° under a reflux condenser, the values obtained were:

Acetic acid	$N/10$-$AgNO_3$ required, c.c.	CN_2H_2 unchanged.	Acetic acid	$N/10$-$AgNO_3$ required c.c.	CN_2H_2 unchanged.
In $N/20$	= 50	= 93·7 per cent.	In $N/4$	= 44·6	= 83·7 per cent.
„ $N/10$	= 48·6	= 91·2 „	„ $N/2$	= 41·6	= 78·1 „

Fifty c.c. of cyanamide solution in normal acetic acid after boiling for ten hours under a reflux condenser required for 5 c.c., 19·6 c.c. $N/10$-$AgNO_3$; unchanged cyanamide = 36·5 per cent.; this result represents the maximum change reached in the experiments in the presence of acetic acid.

In referring to the stability of cyanamide in the solid state, Morrell and Burgen have shown that a specimen after six months still contained 91·1 per cent. of the substance unchanged. A specimen of cyanamide, crystallised from ethereal solution, has given the author, after ten months, the following result:

0·1165 required 51·75 c.c. $N/10$-ammonical silver nitrate; cyanamide = 93·28 per cent.

It is evident, therefore, that the pure substance is much more

stable in the solid state than is generally supposed. On the other hand, a 4 per cent. aqueous solution, after keeping for the same period in a stoppered bottle of clear, white glass, was found to have developed a distinct alkaline reaction towards phenolphthalein, and contained only 20·2 per cent .of the cyanamide unchanged, whilst a few crystals of dicyanodiamide (m. p. 205°) had separated. A determination of the solubility of dicyanodiamide in water at 15° gave 2·56 grams in 100 c.c.

Action of Nitrous Acid on Cyanamide.

The experiments were made in a Lunge nitrometer. A normal solution of cyanamide was used, since on the basis of the equation:

$$CN\cdot NH_2 + HNO_2 = N_2 + H_2O + HCNO$$

1 c.c. should be capable of giving 22·36 c.c. of gas at 0° and 760 mm.

Expt. I.—One c.c. of the cyanamide solution and 0·069 gram of sodium nitrite,* dissolved in 0·5 c.c. of water, were introduced into the nitrometer over mercury, and 1 c.c. of dilute sulphuric acid (1:10) was added. Gas was rapidly evolved, which amounted to 12 c.c. at 18° and 769 mm. after two minutes; at the end of this short interval the evolution of gas diminished considerably, and after one hour 23·8 c.c. were obtained at the same temperature and pressure. The composition of the gas was N = 64·8; CO_2 = 26·4; NO = 8·8 per cent.

An analysis of the gas evolved in the first two minutes showed the presence of 86·3 per cent. of nitrogen.

Since, on account of the hydrolysis of the cyanic acid produced, no useful information was to be obtained by correcting the gas to the normal temperature and pressure, this was not done.

In a repetition of the experiment the residual solution, after the expulsion of the evolved gas, required 10·7 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 53·3 per cent. of that originally present.

Expt. II.—Same proportion as in the previous experiment, but the reaction was allowed to proceed for only twenty minutes.

Volume of evolved gas = 16 c.c. at 15° and 763 mm.; this was not analysed, and was expelled from the nitrometer.

The residual solution required 11·8 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 59 per cent. of that originally present.

Thus approximately 60 per cent. of the cyanamide was unchanged after the completion of the first stage of the decomposition. Whilst this is apparently finished after two or three minutes, the reaction was allowed to continue for twenty minutes

* The specimen of sodium nitrite used was assayed; 0·072 gram was found to be equivalent to 0·069 gram of the pure salt.

on account of the secondary change which no doubt accompanies the primary to a small extent.

Expt. III.—Same proportions as before, but the reactions were allowed to proceed for twenty hours.

Volume of gas evolved = 38·8 c.c. at 16° and 763 mm.

Composition: N = 55; CO_2 = 40·1; NO = 4·9 per cent.

The large increase in the proportion of carbon dioxide shows that the cyanic acid generated was hydrolysed as fast as cyanamide was being attacked by the nitrous acid, after the first rapid decomposition had been completed.

The residual liquid required 2·55 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 12·7 per cent. of that originally present. The remarkable resistance of cyanamide to further attack by nitrous acid, after the first rapid action has been completed as shown by these experiments, suggests that the change $C(NH)_2 \longrightarrow CN{\cdot}NH_2$ must proceed at a very slow rate at the ordinary temperature even in the presence of a dilute mineral acid.

The possible formation of a nitroso-derivative as an intermediate product has yet to be investigated.

The Hydrolysis of Cyanamide.

A 4·25 per cent. solution of cyanamide in ether saturated with water, after keeping for three weeks at the ordinary temperature, and after heating at 100° for ten hours in a sealed tube of soft glass, was found to have suffered no change. After the addition of a few drops of concentrated nitric acid crystals of urea nitrate were slowly deposited. In order to examine the course of this change, the following experiments were made.

Expt. IV.—To 15 c.c. of the moist ethereal solution of cyanamide (0·638 gram CN_2H_2), 1·5 grams of nitric acid (D^{15} 1·425) were added. This was slightly more than sufficient to form urea nitrate by the hydrolysis of all the cyanamide present. After two hours crystals commenced to separate, and the product was kept for twenty hours.

Weight of crystals deposited = 1·9 grams. Theory for urea nitrate = 1·87 grams. All the cyanamide had disappeared from the ethereal solution. The hydrolysis was therefore complete, although it should be mentioned that the crystals contained a small quantity of dicyanodiamidine nitrate.

Expt. V.—The last experiment was repeated, but only 1 gram of nitric acid was added.

Weight of crystals deposited after twenty hours = 1·57 grams.

The residual ethereal solution was shaken with 400 c.c. of distilled water, and then required 63 c.c. *N*/10-ammoniacal silver

nitrate for the complete precipitation of the remaining cyanamide, which is thus found to be 20·7 per cent. of the amount originally present.

Thus whilst all the nitric acid was removed as urea nitrate, the excess of cyanamide remained unchanged, although there was more water present than was necessary to effect its complete hydrolysis.

The remarkable stability of cyanamide and its indifference towards hydrolysis were shown by the following striking and conclusive result.

Expt. VI.—0·42 Gram of cyanamide was dissolved in 20 c.c. of moist ether, and 1 c.c. of fuming hydrochloric acid (D=1·16) added; the mixture was repeatedly shaken in a small stoppered separating funnel during an interval of six hours, and was then kept until the following morning. The small aqueous layer was removed, and after neutralisation with an excess of aqueous ammonia, the cyanamide was precipitated in the form of its silver salt.

Weight of Ag_2CN_2 obtained=1·742; CN_2H_2=0·2856.

The ethereal solution required 46·1 c.c. *N*/10-ammoniacal silver nitrate; CN_2H_2=0·0968. Hence 0·3824 gram, or 91·04 per cent. of the cyanamide originally taken, was unchanged.

Thus, whilst in this experiment the amount of hydrochloric acid present was sufficient to form urea hydrochloride by the hydrolysis of the cyanamide, the amount of water present was too great to allow the undissociated urea salt to separate, and hence very little, if any, hydrolysis of cyanamide took place. A small quantity of dicyanodiamidine was found in the aqueous layer.

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[*Received, April 13th*, 1915.]

LXXVII.—*Steric Influence: Static and Dynamic. Part II.*

By OLIVER CHARLES MINTY DAVIS and
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IN a previous communication (Davis, *Zeitsch. physikal. Chem.*, 1912, **78**, 353) the results of an investigation on the interaction of formic acid with aniline and its congeners were described, the reaction being expressed by the general equation:

$$H\cdot CO_2H + R\cdot NH_2 \rightleftharpoons R\cdot NH\cdot COH + H_2O.$$

In such a system it is possible to measure under suitable conditions:

(1) The velocity of formation of the anilide.

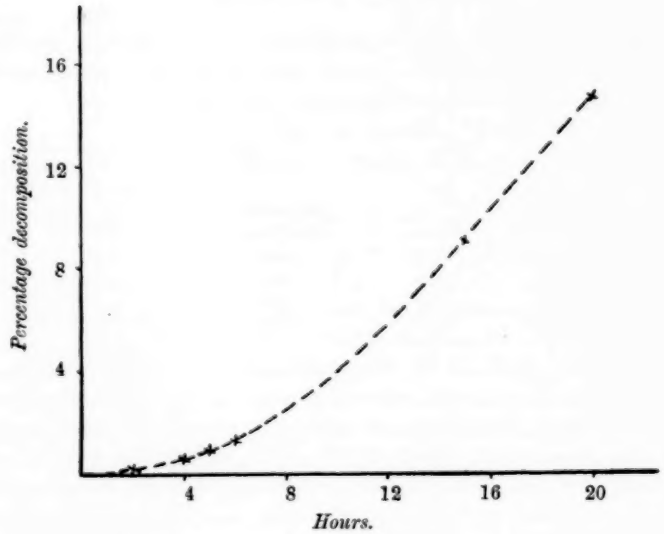
(2) The velocity of decomposition of the anilide.

(3) The position of the point of equilibrium obtained by a direct method.

The research described dealt almost exclusively with the third possibility above mentioned, and numerous equilibrium points were determined by a static method. The main object of the present investigation was to obtain three independent sets of data by a study of the measurements enumerated above, with a view of

FIG. 1.

Decomposition of formanilide.



comparing their relative value, as applied particularly to steric influence. In order to enable such a comparison to be made, the three sets of data have been determined, working under conditions as similar as possible in all cases.

Experimental Conditions.—A solvent was employed consisting of two volumes of pyridine and one of water, this solvent giving homogeneous solutions. The temperature of reaction was that of boiling water, variations due to barometric changes being of no importance.

Preliminary experiments were made with solutions of the following concentrations:

Rate of Formation.—One gram-molecule of formic acid and 1 gram-molecule of aniline per litre.

Rate of Decomposition.—One gram-molecule of the anilide and 1 gram-molecule of water per litre.*

The measurement of rates of formation and equilibria in such solutions could be carried out satisfactorily, but the determination of the rates of decomposition were not completely successful. The following table and curve show the results obtained for the decomposition of formanilide.

Time in hours.	Per cent. decomposed.
2	0·26
3	0·51
5	1·09
6	1·34
15	9·1
20	14·83

The reaction appears to be catalysed by one of the reaction products, and the addition of formic acid produces a considerable increase in the initial rate of decomposition, thus:

Substance.	Hours.	Per cent. decomposed. Molecular solution.	Per cent. decomposed. After the addition of 0·1 gram-mol. of formic acid.
Formanilide	2	0·26	3·45
	3	0·51	4·77
Formo-*o*-toluidide	3	0·53	3·8
	6	1·14	6·21

This effect is confined to the decomposition measurements, a similar excess of acid in the other determinations producing alterations which could be attributed normally to the increase in the mass of the formic acid; thus in the reaction between aniline and formic acid 59·2 per cent. of the anilide was formed in molecular solution, whilst with an excess of the acid as stated, the formation was 62·38 per cent.

The solutions used throughout the following experiments were made up as follows:

Rate of Formation.—Aniline or derivative, 1 gram-mol. per litre, and formic acid, 1·1 gram-mol. per litre.

Rate of Decomposition.—Formanilide or derivative, 1 gram-mol. per litre; formic acid, 0·1 gram-mol. per litre; and water, 1 gram-mol. per litre (in addition to water present in the solvent).

* This water is in addition to that already present in the solvent.

Experimental.

Rate of Formation.—The aniline or derivative was weighed into a stoppered measuring flask, a weighed quantity of standardised formic acid solution in the pyridine–water solvent was added, the required volume made up with the solvent, and the flask weighed. Of this solution one portion was weighed in a stoppered flask and titrated with $N/10$-sodium hydroxide, and six other portions were placed in tubes of Jena-glass, previously steamed. These tubes, closed by corks having narrow grooves cut in them,* were heated on a water-bath, being supported in the lid of the bath by enlargements on the tubes.

At intervals of fifteen minutes a tube was taken out and rapidly cooled, and the contents were poured into a stoppered flask, weighed, and titrated.

Rate of Decomposition.—The method adopted for making the solution was that described above. A portion of the solution having been titrated, the remainder was heated in a Jena flask fitted with a ground-in reflux condenser. Portions of the solution were removed by a pipette every hour, rapidly cooled, weighed, and titrated.†

Equilibrium.—Portions of the solutions prepared for the above determinations were sealed in glass tubes, the method used being that described by Davis (*loc. cit.*).

Treatment of Data.—Empirical formulæ have been used to calculate the constants, giving fairly consistent results, as will be seen from the table which follows. Water being present in comparatively large quantity, a practical constancy in its amount has been assumed in calculating the decomposition constant and the equilibrium constant.

The formulæ used are:

Formation:

$$k_1 = \frac{1{\cdot}4}{t(b-a)(b-x)} \log \frac{a}{b} \frac{(b-x)}{(a-x)},$$

where t = time in minutes, a = concentration of the aniline or derivative = 1, b = concentration of the formic acid = 1·1, and x = amount of the anilide formed.

Decomposition:

$$k_2 = \frac{1}{t(a-b)} \log \frac{a(b+x)}{b(a-x)},$$

where a = concentration of the anilide or derivative = 1, b = concen-

* The loss due to volatilisation was found to be negligible.

† A slight variation was introduced, the formic acid solution and the water being measured into the flask instead of being weighed.

tration of the formic acid = 0·1, x = amount of the anilide decomposed in t minutes.

Equilibrium:

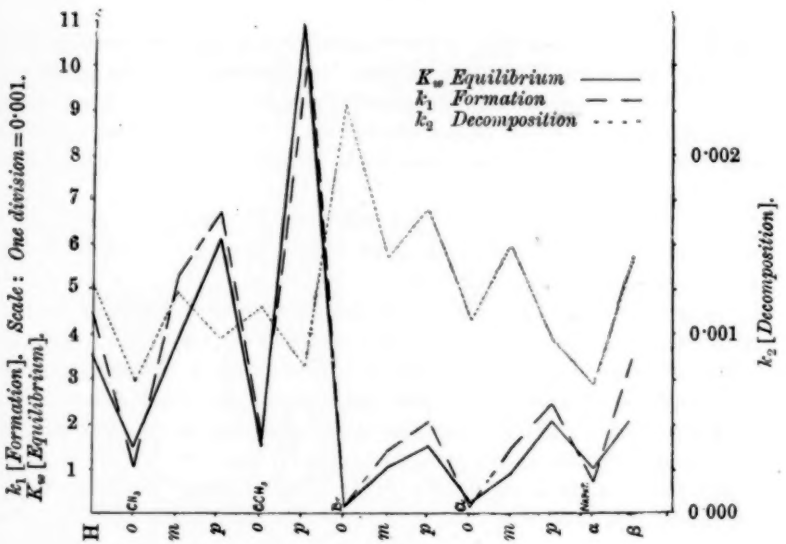
$$K_w = \frac{a}{b+c},$$

where a, b, c are the concentrations of the anilide or derivative, aniline or derivative, and formic acid respectively.

Discussion of Results.

It is possible to compare the results in two distinct ways; either the effect of the position of a single substituent group may be

FIG. 2.



considered, or the result of substituting different groups in the same position may be taken as a basis of comparison.

It will be seen by consulting the table already given or the one following that the rates of formation and the percentage of substance formed run approximately parallel, and that the values in the case of ortho-, meta-, and para-isomerides increase in the order mentioned, the increase being particularly pronounced for *o*- and *m*-halogen-substituted derivatives.

No such regularity is found in the rates of decomposition.

Referring to the effects of the various groups when substituted in similar positions, it may be said that it is difficult to arrange

	Average k_1.	Maximum difference of any constant from average.	Average k_2.	Maximum difference of any constant from average.*	Percentage of anilide at equilibrium point.	$K_{25°}$.	k_1/k_2.
Formanilide	0·0045	0·0004	0·0013	0·0001	62·38	3·55	3·46
Formo-*o*-toluidide	0·00108	0·00005	0·00072	0·00007	48·12	1·50	1·49
Formo-*m*-toluidide	0·0053	0·0007	0·0012	0·00006	64·5	3·99	4·4
Formo-*p*-toluidide	0·0067	0·0003	0·00094	0·00004	70·63	6·11	7·1
Formo-*o*-anisidide	0·0018	0·0001	0·00116	0·0001	48·2	1·50	1·55
Formo-*p*-anisidide	0·0099	0·0004	0·00083	0·0001	77·9	11·0	11·9
o-Bromoformanilide	0·00028	0·0001	0·0023	0·0005	10·5	0·12	0·13
m-Bromoformanilide	0·0014	0·00007	0·0014	0·0003	41·0	1·01	1·0
p-Bromoformanilide	0·0021	0·0001	0·0017	0·0001	49·5	1·62	1·29
o-Chloroformanilide	0·00013	0·00008	0·0011	0·00001	10·07	0·14	0·12
m-Chloroformanilide	0·00154	0·00004	0·0015	0·0002	39·3	0·90	1·0
p-Chloroformanilide	0·0025	0·0002	0·00094	0·00003	53·8	2·07	2·6
Formo-α-naphthalide	0·00072	0·00002	0·00072	0·00004	41·0	1·01	1·0
Formo-β-naphthalide	0·0036	0·0005	0·0014	0·0001	54·8	2·20	2·57

* The rather large maximum difference from the average is given always by the first result, the reason for this being probably the catalytic action which has already been discussed.

them in order of influence. In the ortho-positions they may be ordered thus: β-ring, O·CH_3, CH_3, α-ring, Br, Cl.*

In the meta- and para-positions the effect of the halogen atoms is in the reverse order. Stress cannot be laid on this owing to the slight differences in the numbers obtained for these particular substances, especially in the case of the ortho- and meta-isomerides.

The rates of decomposition do not lend themselves to any ordered comparison.

Further comparisons may be readily made by the aid of the table on p. 735.

Conclusion.

Equilibrium measurements applied to a reaction or series of reactions give more reliable results than do the determinations of either the rates of formation or decomposition, and should be, if possible, selected for the investigation of a reaction provided it is only intended to make one type of observation. On the other hand, the comparison of velocity measurements with equilibrium data gives, with regard to the mechanism of a reaction, much more complete and valuable information, which may probably be used to discriminate between the various factors in the reaction.

Note by F. W. Rixon.

Factors of the Reactions.

In the formation and the decomposition of the anilides the steric influence is one factor, the chemical effect of the substituent may be regarded as a second, and the action of the formic acid as a third; there may be other factors, but these three are obvious.

If H represents a factor compounded of the first and second, whilst F represents the third, the formation of a substance may be expressed thus:

$$k_1 \alpha F/H,$$

and its decomposition by:

$$k_2 \alpha FH.$$

By combining these two relations, the factor F, which would be supposed to have equal accelerative effect on both reactions, can be eliminated, and

$$H^2 k_1 \alpha k_2 \text{ or } H^2 \alpha\, k_2/k_1.$$

* The α- and β-rings are included, although the inclusion can hardly be justified; this remark applies equally to other comparisons that are made in which the α- and β-rings are involved.

Comparative Table of Results, in which the values obtained for Formanilide are taken as Unity.

k_1 = Formation.
k_2 = Decomposition.
% = Amount of anilide at equilibrium point.

Position of Group.	CH_3.			$O{\cdot}CH_3$.			Br.			Cl.			α-Ring.			β-Ring.		
	k_1	k_2	%	k_1	k_2	%	k_1	k_2	%	k_1	k_2	%	k_1	k_2	%	k_1	k_2	%
o	0·25	0·55	0·76	0·4	0·89	0·77	0·06	1·7	0·17	0·03	0·84	0·16	0·16	0·55	0·65	0·8	1·07	0·88
m	1·2	0·92	1·03				0·31	1·07	0·65	0·34	1·15	0·63						
p	1·5	0·72	1·13	2·0	0·64	1·24	0·47	1·3	0·79	0·55	0·72	0·86						

Making this assumption, the values of H may be expressed proportionally in round numbers as follows:

Group.	*o*.	*m*.	*p*.	Ring.
CH_3	15	9	7	α 19
$O{\cdot}CH_3$	15	—	6	—
Br	53	19	17	β 9
Cl.....	53	18	13	—

These numbers are merely proportional, and are derived, in the manner indicated, from the table in which the parent substance formanilide is the unit.

The similar results obtained from the halogens point to the conclusion that the extra weight of the bromine atom is counterbalanced by the chemical activity of the chlorine, the two atoms exercising an equal hindering effect.

If steric influence is proportional to the weight of the substituent group, the factor H might be divided by the weight of the group in question; the quotient would be a proportional representation of what might be termed "chemical hindrance."

The above method of treatment is purely tentative, and is suggested as possibly allowing a direct comparison to be drawn between the effects produced by substituting different groups in a reacting system, and a discrimination to be made between certain of the reaction factors.

The expenses in connexion with the work have been partly met by a grant from the Royal Society, for which the authors express their thanks.

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[*Received, February 20th*, 1915.]

LXXVIII.—*Heneicosoic Acid.*

By HENRY RONDEL LE SUEUR and JOHN CHARLES WITHERS.

ALL the normal acids of the acetic series up to and including the acid containing twenty-two carbon atoms, with the exception of the acid with twenty-one carbon atoms, have been prepared and described, and we thought it would be interesting to attempt the preparation of the missing acid by the reduction of μ-ketoheneicosoic acid, $CH_3{\cdot}[CH_2]_7{\cdot}CO{\cdot}[CH_2]_{11}{\cdot}CO_2H$, which we had obtained in considerable quantities, as described in a former communication (T., 1914, **105**, 2800). We find that this ketonic acid is

easily and almost quantitatively reduced to the corresponding unsubstituted normal acid by boiling it with amalgamated zinc and hydrochloric acid (Clemmensen, *Ber.*, 1913, **46**, 1837; 1914, **47**, 51, 681). Clemmensen's method appears to be particularly suitable for the reduction of ketonic acids of this type, for we also find that θ-ketomargaric acid, $C_8H_{17}\cdot CO\cdot[CH_2]_7\cdot CO_2H$ (T., 1914, **105**, 2800), is readily reduced to margaric acid, $C_{16}H_{33}\cdot CO_2H$, by this method.

The work described in this communication and in that previously referred to shows that it is comparatively easy to pass from a higher, unsaturated acid to the saturated acid containing one carbon atom less, the series of changes in the case of the preparation of margaric acid from oleic acid being as follows:

$$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H \xrightarrow[KMnO_4]{\text{alkaline}}$$

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H \xrightarrow[\text{with KOH}]{\text{fusion}}$$

$$CH_3\cdot[CH_2]_7\cdot C(OH)(CO_2H)\cdot[CH_2]_7\cdot CO_2H \xrightarrow{KMnO_4}$$

$$CH_3\cdot[CH_2]_7\cdot CO\cdot[CH_2]_7\cdot CO_2H \xrightarrow{\text{reduction}} CH_3\cdot[CH_2]_7\cdot CH_2\cdot[CH_2]_7\cdot CO_2H.$$

More than fifty years ago Eylerts (Wittstein's *Vierteljahrsschrift pr. Pharm.*, 1860, **9**, 330) stated that he had isolated from beef-marrow an acid melting at 72·5°, to which he gave the name medullic acid and the formula $C_{21}H_{42}O_2$. Mohr (*Zeitsch. physiol. Chem.*, 1890, **14**, 390) and Thummel (*Arch. Pharm.*, 1890, **228**, 280) showed that Eylerts' medullic acid was stearic acid, and that the solid acids in beef-marrow consist of stearic and palmitic acids only. Unfortunately, Eylerts did not prepare any derivatives of his acid, so that we are unable to say whether the acid he isolated was identical with the one described in the present communication, but from the work of Mohr and Thummel, and also from the fact that the higher fatty acids with an odd number of carbon atoms seldom, if ever, occur in nature, it would appear that the so-called medullic acid had not the composition assigned to it.

Experimental.

Preparation of Heneicosoic Acid, $CH_3\cdot[CH_2]_{19}\cdot CO_2H$.

Fifty grams of commercial granulated zinc were kept immersed in a 1·25 per cent. solution of mercuric chloride for one hour; the liquid was then poured off, and the amalgamated zinc introduced into a flask in which were 5 grams of μ-ketoheneicosoic acid and 50 c.c. of concentrated hydrochloric acid. The flask was

attached to a reflux condenser, and the contents were boiled for seven hours, during which time five lots of 5 c.c. of concentrated hydrochloric acid were added at regular intervals. The contents of the flask were allowed to cool, the liquid was poured away from the solidified acid, and a fresh quantity of 50 c.c. of concentrated hydrochloric acid added, and the boiling continued for another seven to eight hours. When cold, the aqueous liquid was poured away, and a fresh quantity of 50 grams of amalgamated zinc and 50 c.c. of concentrated hydrochloric acid added, and the heating continued for another eight hours. Finally, the aqueous liquid was again replaced by a fresh quantity of 50 c.c. of concentrated hydrochloric acid, and the mixture boiled for eight hours longer; in all cases, quantities of 5 c.c. of hydrochloric acid were added after about every two hours' interval. When cold, the solid acid was dissolved in ether, the ethereal solution washed, dried, and evaporated, and the residue crystallised from acetone until its melting point was constant. The yield was 90 per cent. of the theoretical:

0·1116 gave 0·3157 CO_2 and 0·1314 H_2O. C = 77·15; H = 13·18.
0·3530 required 10·8 c.c. 0·1*N*-NaOH. M.W. = 326·8.
$C_{21}H_{42}O_2$ requires C = 77·22; H = 12·97 per cent. M.W. = 326·3.

Heneicosoic acid, $CH_3{\cdot}[CH_2]_{19}{\cdot}CO_2H$, is readily soluble in ether, chloroform, or benzene in the cold, and in hot ethyl acetate or acetone, and crystallises from the latter solvent in stellar aggregates of stout needles, melting at 73—74°. The white *silver* salt was obtained on adding a solution of the sodium salt to a solution of silver nitrate:

0·1104 gave 0·0272 Ag. Ag = 24·64.
$C_{21}H_{41}O_2Ag$ requires Ag = 24·90 per cent.

Methyl heneicosoate, $CH_3{\cdot}[CH_2]_{19}{\cdot}CO_2Me$, was prepared by heating the dry silver salt of the acid with methyl iodide dissolved in benzene, and was purified by crystallisation from methyl alcohol. It is readily soluble in cold ether, benzene, or chloroform, and also in hot acetone or methyl alcohol, and separates from the latter solvent in thin, lustrous scales, melting at 49°:

0·1106 gave 0·3138 CO_2 and 0·1304 H_2O. C = 77·38; H = 13·19.
$C_{22}H_{44}O_2$ requires C = 77·57; H = 13·03 per cent.

Heneicosoamide, $C_{20}H_{41}{\cdot}CO{\cdot}NH_2$, was prepared thus: 1 gram of heneicosoic acid and 1 gram of thionyl chloride were heated together, first on the water-bath and then over wire gauze, until the action had ceased. The product was diluted with ether and poured into concentrated ammonia, and then the precipitated amide was collected, washed, and crystallised from acetone, when

it was obtained as aggregates of needles, melting at 110°. It is insoluble in ether, and dissolves readily in warm alcohol, acetone, or benzene:

0·2839 gave 10·9 c.c. N_2 at 15° and 748 mm. N = 4·43.
$C_{21}H_{43}ON$ requires N = 4·31 per cent.

α-Bromoheneicosoic acid, $C_{19}H_{39}\cdot CHBr\cdot CO_2H$, was prepared in the usual way by adding bromine to the acid chloride obtained by the action of phosphorus pentachloride on heneicosoic acid. The crude bromo-acid chloride was decomposed by heating with water, and the resulting bromo-acid was crystallised from light petroleum, from which it separates in groups of slender needles, melting at 65·5—66·5°. It is sparingly soluble in light petroleum or glacial acetic acid, and dissolves readily in ether, alcohol, or chloroform in the cold:

0·2913 required 7·2 c.c. 0·1*N*-$AgNO_3$. Br = 19·75.
$C_{21}H_{41}O_2Br$ requires Br = 19·72 per cent.

α-Hydroxyheneicosoic acid, $C_{19}H_{39}\cdot CH(OH)\cdot CO_2H$, was obtained from the corresponding bromo-acid by boiling it for twenty-eight hours with a 5 per cent. solution of potassium hydroxide. The crude acid was purified by crystallisation from chloroform, from which it separated in aggregates of needles, melting at 93—94°. It is sparingly soluble in alcohol, ether, chloroform, benzene, or acetone in the cold, but readily dissolves on heating. When heated at about 280°, it behaves like all the other α-hydroxy-derivatives of the higher fatty acids in that it readily loses carbon monoxide (T., 1904, **85**, 827; 1905, **87**, 1788):

0·1206 gave 0·3245 CO_2 and 0·1351 H_2O. C = 73·38; H = 12·54.
$C_{21}H_{42}O_3$ requires C = 73·61; H = 12·37 per cent.

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[*Received, May 5th*, 1915.]

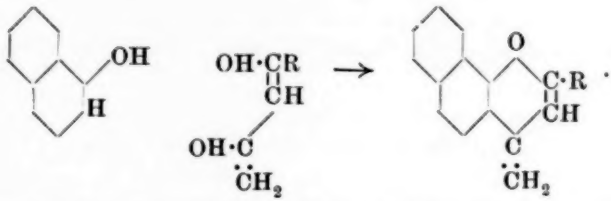
LXXIX.—*Synthesis of α-Naphthapyranoles.*

By BROJENDRA NATH GHOSH.

BÜLOW, in a series of papers (Bülow and Wagner, *Ber.*, 1901, **34**, 1189; Bülow, *ibid.*, 1903, **36**, 190; Bülow and Deiglmayr, *ibid.*, 1904, **37**, 1791; Decker and Becker, *ibid.*, 1914, **47**, 2288), has shown that diketones, such as acetylacetone or benzoylacetone, condense with resorcinol, pyrogallol, and phloroglucinol to yield

the corresponding benzopyranol derivatives, whilst Collie and White (T., 1915, **107**, 369) have also obtained similar compounds with acetylacetone and orcinol.

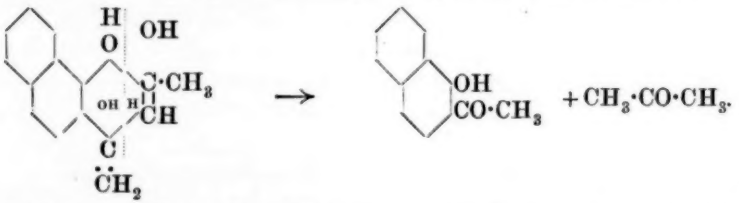
The author and Jacobson have recently shown (T., 1915, **107**, 424) that the behaviour of α-naphthol is exactly similar to that of *m*-dihydroxyphenols in the formation of benzo-γ-pyrones, and further evidence of this similarity has now been sought in the formation of pyranols. It is shown in the present paper that α-naphthapyranol may be synthesised from acetylacetone or benzoylacetone and α-naphthol, the reaction being expressed as follows:



Some further interest is attached to the naphthapyranols on account of the fact that the naphthapyranol structure has been ascribed to the lapachan group of natural dyes.

In the present work, the condensing agent used was phosphoryl chloride in preference to hydrogen chloride, which was employed by the previous investigators in synthesising members of this group. It is found that this condensing agent acts more rapidly and gives better yields. Sen-Gupta (T., 1914, **105**, 399) has also observed that phosphoryl chloride acts as a better condensing agent than hydrochloric acid in condensing ketones with phenols.

The constitution of the product was proved by fusion with alkali hydroxide, which yielded 1-hydroxy-β-naphthyl methyl ketone. The decomposition may be represented as follows:



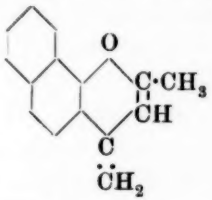
Collie and White (*loc. cit.*) have suggested that the colour of the compounds obtained from *m*-dihydroxyphenols and these diketones might be due to a quinonoid structure. This view is supported by the fact that the substances now described, to which a quinonoid arrangement cannot be assigned, are almost colourless.

Both these substances form the well-defined, characteristic salts

peculiar to this group. Some of these salts have been isolated and analysed.

Experimental.

2-Methyl-4-methylene-1 : 4-α-naphthapyranol.



Seven grams of α-naphthol and 5 grams of acetylacetone were added to 2—3 c.c. of phosphoryl chloride, and the mixture was heated during about a quarter of an hour at 100—105°, hydrogen chloride being evolved. After being cooled, the viscous mass was dissolved in alcohol, and the solution was treated with an excess of aqueous sodium acetate, when the above substance separated as a reddish-coloured, amorphous precipitate. In order to purify this product, it was dissolved in a small quantity of acetic acid, and water was added to the solution, when a dark-coloured impurity was precipitated, and the solution remained almost colourless. The precipitate was removed, and the clear solution was treated with an excess of dilute sodium hydroxide, when the product was precipitated in an almost colourless condition. It was crystallised from acetone by carefully adding a few drops of water to the solution:

0·1035 gave 0·3136 CO_2 and 0·0583 H_2O. C = 82·9; H = 6·3.
$C_{15}H_{12}O,\frac{1}{2}H_2O$ requires C = 83·3; H = 6·4 per cent.

The water of crystallisation was estimated by keeping the substance at 100° for three hours:

0·3610 lost 0·0148. H_2O = 4·1.
$C_{15}H_{12}O,\frac{1}{2}H_2O$ requires H_2O = 4·1 per cent.

2-Methyl-4-methylene-1 : 4-α-naphthapyranol forms pale, buff-coloured needles which, when heated in a capillary tube, change colour at about 150°, and melt and decompose at 166°. It is almost insoluble in alcohol or water, but is soluble in acetic acid, pyridine, chloroform, or xylene. In concentrated sulphuric acid it dissolves with a brown colour, and develops an intensely green fluorescence. A solution of the substance in acetone decolorises alkaline permanganate. On keeping the substance in air it changes its colour, and slowly turns green.

The *picrate* was prepared by mixing saturated solutions of the

components in xylene. It crystallises in yellowish-green needles, which melt and decompose at 159°:

0·1998 required 4·6 c.c. $N/10$-NaOH. $C_6H_3O_7N_3 = 52·8$.
$C_{15}H_{12}O,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3 = 52·4$ per cent.

The *mercurichloride* was prepared in the same way as the picrate. It formed a yellowish-brown precipitate, which did not melt, but decomposed at a high temperature:

0·1417 gave 0·0688 HgS. Hg = 41·8.
$C_{15}H_{12}O,HgCl_2$ requires Hg = 41·7 per cent.

The *perchlorate* was prepared by dissolving a small quantity of the substance in aqueous perchloric acid. It decomposes with explosive violence on heating:

0·2426 required 7·5 c.c. $N/10$-NaOH. $HClO_4 = 31·0$.
$C_{15}H_{12}O,HClO_4,H_2O$ requires $HClO_4 = 30·9$ per cent.

The *platinichloride* was prepared by mixing a solution of chloroplatinic acid with a warm solution of the substance in hydrochloric acid, and was deposited as a yellow, crystalline precipitate:

0·1154 gave 0·0262 Pt. Pt = 22·5.
$(C_{15}H_{12}O)_2,H_2PtCl_6,2H_2O$ requires Pt = 22·2 per cent.

The *aurichloride*, prepared by adding to an ethereal solution of the substance a solution of chlorauric acid in the same solvent, is a dark brown, crystalline powder:

0·0840 gave 0·0166 Au. Au = 19·7.
$(C_{15}H_{12}O)_3,HAuCl_4,3H_2O$ requires Au = 19·3 per cent.

The *hydrochloride*.—On passing a current of dry hydrogen chloride into a solution of the substance in dry chloroform, an oily product separated, which could not be obtained crystalline. On keeping a solution of the pyranol in concentrated hydrochloric acid in a vacuum over sodium hydroxide, a yellow, crystalline compound was obtained, which melted and decomposed at 96°:

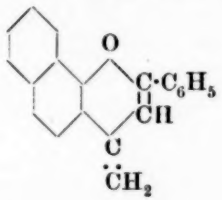
0·1842 required 7·1 c.c. $N/10$-NaOH. HCl = 14·0.
$C_{15}H_{12}O,HCl,H_2O$ requires HCl = 13·7 per cent.

Interaction of the Pyranol and Potassium Hydroxide.

In order to prove the constitution of the substance, 3 grams of the pyranol were fused with 15 grams of potassium hydroxide dissolved in a little water, for about five minutes. After being cooled, the fusion was dissolved in water, and the insoluble matter was separated by filtration. On passing a current of carbon dioxide through the solution, a white, crystalline precipitate separated, which was collected and washed. The product crystal-

lises from dilute alcohol in colourless needles, melting at 103°. The identity with 1-hydroxy-β-naphthyl methyl ketone (m. p. 103°) was confirmed by the melting point of its acetyl derivative.

2-Phenyl-4-methylene-1 : 4-α-naphthapyranol,



This was prepared by heating a mixture of 7 grams of α-naphthol, 8 grams of benzoylacetone, and 2—3 c.c. of phosphoryl chloride at 100—105° during about an hour. The product was treated as in the case of the preceding naphthapyranol. It was recrystallised by carefully adding a few drops of water to the solution in pyridine. It changes colour on heating at about 115°, but melts and decomposes at 125°. In sulphuric acid it develops a green fluorescence:

0·1240 gave 0·3800 CO_2 and 0·0604 H_2O. C = 83·5; H = 5·4.
$C_{20}H_{14}O,H_2O$ requires C = 83·3; H = 5·5 per cent.

The *picrate* was prepared by mixing solutions of the constituents in xylene. It forms yellowish-green, crystalline needles, which melt at 165°:

0·2218 required 4·4 c.c. *N*/10-NaOH. $C_6H_3O_7N_3$ = 45·4.
$C_{20}H_{14}O,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$ = 45·8 per cent.

The *mercurichloride*, prepared in the same way, was obtained as a brown, amorphous powder:

0·1538 gave 0·0892 HgS. Hg = 50·0.
$C_{20}H_{14}O,HgCl_2$ requires Hg = 50·0 per cent.

The *perchlorate* was prepared by adding perchloric acid (D 1·49) to an acetic acid solution of the substance, when it crystallised in long, green needles. It was collected, washed with acetic acid, and kept in a vacuum over sodium hydroxide. On heating, it deflagrates with explosive violence:

0·2274 required 5·7 c.c. *N*/10-NaOH. $HClO_4$ = 25·2.
$C_{20}H_{14}O,HClO_4,H_2O$ requires $HClO_4$ = 25·7 per cent.

The *platinichloride* was obtained in the form of brown needles:

0·2611 gave 0·0676 Pt. Pt = 25·8.
$(C_{20}H_{14}O)_2,H_2PtCl_6$ requires Pt = 25·9 per cent.

I take this opportunity of expressing my sincere gratitude to Dr. Smiles for the interest he has taken in the work.

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[*Received, April 19th,* 1915.]

LXXX.—*The Valency Volume Theory.*

By THOMAS VIPOND BARKER.

THE valency volume theory of Barlow and Pope has attracted a considerable amount of attention on account of its apparent success in correlating the intimately connected subjects of crystal form and chemical structure. As regards its more chemical aspects, the theory has been recently examined by Richards (*J. Amer. Chem. Soc.*, 1913, **35**, 382; 1914, **36**, 1686), who has indicated, amongst many other interesting matters, that the interpretation given by Le Bas (T., 1907, **91**, 112) of Krafft's work on the molecular volumes of a large number of paraffins has no conclusive bearing on the subject of valency volumes. The present criticism is chiefly directed towards the crystallographic features of the theory, with especial reference to an examination of the alleged quantitative evidence, which has from time to time been collected by the numerous adherents of the theory in its support. It may be said at once that, as a result of an exhaustive examination of this evidence, the writer has arrived at the conclusion that the data derived from the angular measurements of crystals afford no ground for supposing that the theory is in accordance with facts, and that the apparently satisfactory results obtained by the authors of the theory and their followers have been due to the subsequent application to the observed data of arithmetical operations, which are arbitrary and inadmissible, and might have been equally used to produce similar results from quite other assumptions.

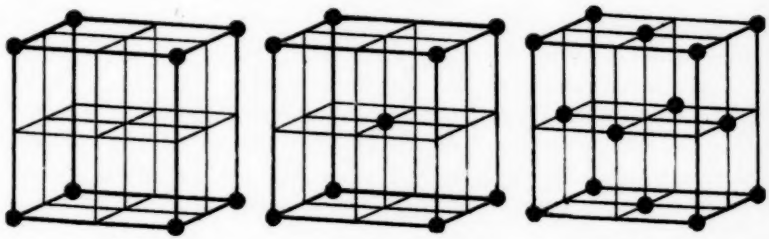
It is found convenient to divide the paper into three principal parts: the first (p. 745) deals with the fundamental assumption on which the theory is based; the second (p. 748) is occupied with an examination of the methods employed by the authors in testing the theory in the light of the crystallographic facts; the third (p. 765) is devoted to an account of certain objective

methods of criticising crystallographic data and to a systematic and detailed examination of the more cogent individual pieces of evidence in the light of these methods.

Part I.—*Deduction of the Law of Valency Volumes.*

The train of reasoning which led to the deduction of the law of valency volumes is indicated by the authors in the introductory pages of their first memoir (T., 1906, **89**, 1678) in the following words: "The ordinary law of valency is thus merely an interpretation of a simple geometrical property of close-packed homogeneous assemblages of spheres." It is obvious that the validity of this deduction depends primarily on the correctness of the fundamental assumption, namely, that the problem of crystal structure is one of close-packing of spheres. Apparently realising that there is nothing in the geometrical theory of crystal structure which

Fig 1.



(*a*) (*b*) (*c*)

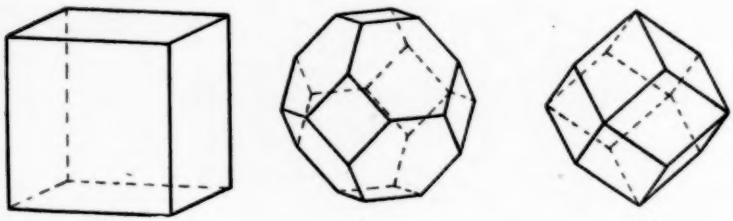
warrants the serious limitation involved in their original assumption, the authors have from time to time sought to advance certain general considerations in its support. It will be well to examine these arguments as applied to the simplest possible case, namely, that of an element crystallising in the cubic system.

The geometrical theory of crystal structure leads to the conclusion that no fewer than three simple structural types or space lattices are available, as well as several more complicated types which need not be considered. The three structures are those known as the simple cubic, centred cubic, and centred-face cubic lattices, respectively, shown in Fig. 1, (*a*), (*b*), and (*c*), in which the points represent the positions of the component atomic centres.

Without going into details, it may be stated that each of these three assemblages corresponds to a space-filling system of cells having the form of the cube, cubo-octahedron, and rhombic dodecahedron, respectively, shown in Fig. 2, (*a*), (*b*), (*c*), for the centres of such polyhedral systems are arranged according to the schemes

shown in Fig. 1. It is, moreover, possible to inscribe spheres in the three polyhedra of Fig. 2, and we may therefore look upon Fig. 1 as alternatively representing the centres either of the polyhedral systems of cells indicated by Fig. 2, or of corresponding assemblages of spheres. With regard to the sphere-assemblages, it may be mentioned that each sphere is in contact with six, eight, and twelve neighbours in the three cases (*a*), (*b*), (*c*), respectively. Now the third assemblage is the one selected by Barlow and Pope as representing the structure of the cubic elements, the basis of the selection being, of course, prompted by the fact that this particular assemblage is packed more closely than the other two. Since, however, the authors admit that the real structure of a crystal is more akin to systems of polyhedral cells than to systems of spheres, and since all three types of polyhedra (*a*), (*b*), and (*c*) fill space absolutely (and therefore equally), it is legitimate to make the following enquiry: What reasons have the authors to

FIG 2.



(*a*) (*b*) (*c*)

offer for the adoption of (*c*) in preference to (*a*) or (*b*)? It must be borne in mind that the example under examination is a typical one, inasmuch as the structures proposed by Barlow and Pope consist in all cases of close-packed spheres.

In the first memoir (p. 1676) the authors state: "The attractive forces acting between the atoms will cause the portions of space which they respectively appropriate, supposed as spherical as possible, to be in contact one with another, at the maximum number of points." In a later memoir (W. Barlow and W. J. Pope: "The Nature of Valency"—Contribution to Discussion in Section B, British Association, Leicester, 1907; pp. 16, privately printed, Manchester, 1907—p. 4) we read: "In the crystalline structure assumed by an element, provided that the identical component atoms do not form groups or molecular aggregates, the constituent atoms of which have diverse situations, the polyhedral spaces appropriated by the atoms will be all alike; the simplest possible assumption which can be made as to the shape of these

spaces or spheres of atomic influence is that they depart as little as possible from sphericity. The polyhedral cells must fill space without leaving interstices, and, according to the assumption referred to, the centres of the identical polyhedral cells will be those of the centre of a closest-packed assemblage of equal spheres." It must here be stated that the conclusion is incorrect; if the spheres of atomic influence do "depart as little as possible from sphericity" (which is not an unreasonable supposition), then the centres of the identical polyhedral cells are represented by (*b*) above, and not by (*c*).

A final quotation may now be permitted ("Contribution to the Second Solvay Conference," Brussels, 1913, p. 8): "We assume that each atom in a crystalline structure acts as a centre of operation of two opposing influences, namely, (*a*), a repellent force, which may be attributed to the kinetic energy of the atoms, and (*b*), an attractive force, both, like gravity, being governed by some inverse distance law. The crystallised assemblage must be premised to be a stable one as a result of an equilibrium set up between the sets of forces thus emanating from the interacting atoms present." Then, in discussing the problem of the elements (*ibid.*, p. 10), the authors proceed: "It is therefore necessary to determine what conditions control the equilibrium arrangement of such a set of identically similar centres of attracting and opposing forces. Consideration will show that if the attention is confined to the interaction between neighbouring atoms, an equilibrium arrangement will result when the condition is fulfilled that, for a given density of packing of the force-centres, the distances separating nearest centres is a maximum"—a condition which is fulfilled by the arrangement (*c*) as compared with (*a*) and (*b*).

The above brief excerpts appear to exhaust the general considerations advanced in support of the fundamental assumption that a crystal edifice is structurally represented by a close-packed sphere-assemblage. It will be seen that there is no attempt at any proof that an assemblage of points corresponding with a close-packed assemblage of spheres is relatively stable as compared with other assemblages; the "considerations" merely indicate a hope, opinion, or conviction that close-packing of spheres is the correct principle to be employed in the reconstruction of a crystal edifice.

In view of the paucity of details (T., 1906, **89**, 1678), it is scarcely possible to criticise the steps involved in the deduction of the "law of valency volumes" from the principle of close-packing. The details given by the authors are, in fact, so meagre that it is impossible to estimate how far there is a mutual interdependence of the "law" and the "principle," or to decide, for example,

whether any ultimate disproof of the law of valency volumes would necessarily carry with it the logical abandoning of the principle of close-packing. The present author is far from being sure that the law of valency volumes does not really involve a second assumption or hypothesis.

It would scarcely be profitable to examine in detail the further assumptions made by the authors in the course of their work, for the reason that the principle of close-packing and the law of valency volumes collectively regulate the mechanical reconstruction of all the crystalline structures examined. We may therefore proceed immediately to the next part of this paper.

PART II.—*An Examination of the Methods Employed by its Adherents in Testing the Theory in the Light of the Crystallographic Facts.*

The crystallographic evidence on which the authors attempt to establish the law of valency volumes is purely geometrical. It is shown that if atomic spheres of appropriate sizes be selected in accordance with the law of valency volumes, then these spheres can be close-packed so as to give a homogeneous assemblage, which is held to be in accordance with the crystalline form of the substance in the following particular: the spacing of the molecular units along three directions selected in the suggested assemblage of spheres is in close correspondence with the axial ratios deduced from goniometrical measurements. In view of the general acceptance of the space lattice as the foundation of the structure of a crystal, there can be no question concerning the legitimacy of this method of attack; its weakness lies in the lack of precision which must always attach to knowledge entirely derived from the purely geometrical aspect of crystallography. The angular relations between the faces of a crystal can usually be represented by "axial ratios" in a variety of ways, owing to a freedom of choice of the axial and parametral faces; in the absence of any ultimate knowledge or of a principle embodying a certain degree of objectivity* (as, for example, the principle adopted by Fedorov in his work on crystallochemical analysis), it has always been held to be legitimate to select any particular set of ratios which appears to be most suitable. Now, it must be noted that, besides making free use of this ambiguity, the adherents of the valency-volume theory do not hesitate to go a step further; in those cases in which the desired correspondence is not so easily forthcoming, the authors

* To admit the absence of such a principle would really be tantamount to acknowledging that we are unable to probe crystal structure from the point of view of goniometrical measurement.

arbitrarily modify the axial ratios by taking fractions or multiples of the axial lengths, the "correct" fractions to be taken being found by an *ad hoc* process of trial. The importance of this matter may be gauged from the estimate that at least 90 per cent. of the whole work is thereby affected. It is obvious, then, that a detailed examination of the various methods adopted by the authors in their interpretation of the geometrical evidence is indispensable to any general estimate of the success which has attended the crystallographic application of the theory.

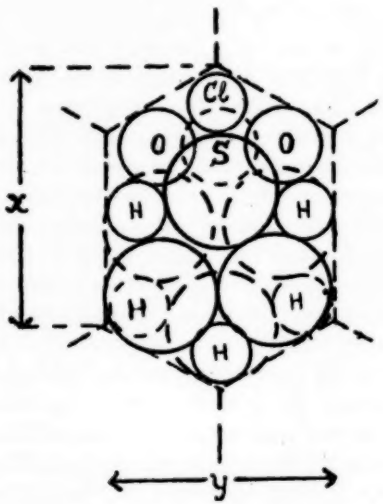
Close-packing.

The representation of a chemical molecule, for purposes of diagrams or models, as an assemblage of spherical atomic components is acknowledged by the authors to be convenient rather than exact, for it is carefully pointed out that the space in a crystal should be regarded as entirely filled with atomic domains of influence, whilst in an assemblage of spheres, on the other hand, there is, of course, much interstitial space. The space-filling, non-spherical domains are conceived as derivable from the original spheres by the operation of an attractive force which deforms the spherical atom without altering its volume. The authors have not, apparently, subjected the effect of this deformation on the relative distances of the atomic centres to a rigorous mathematical analysis, but merely put on record their belief that comparisons between the relative dimensions of the sphere assemblage and the results of goniometrical measurements are quite valid provided that the sphere assemblage is "close-packed." It would appear, however, that this conclusion is not always reasonable.

The authors measure the degree of close-packing by the number of sphere contacts. It must, however, be remembered that the absolute degree of close-packing, that is to say, the ratio of the space occupied by the spheres to the whole space, is largely influenced by the relative sizes of the atom. Thus a sphere of volume two will often fit into a cavity which would not hold two spheres of volume one, and vice versa. It thus comes about that certain parts of a molecule are much more closely packed than others; an excellent example is the structure advocated by Armstrong, Colgate and Rodd for a large series of benzenesulphonyl chlorides (*Proc. Roy. Soc.*, 1914, [*A*], **90**, 118). The diagram is reproduced as Fig. 3, and represents a plan of the structure consisting of two layers of spheres composing a molecule, $C_6H_5 \cdot SO_2Cl$ (or, more generally, $C_6H_3XY \cdot SO_2Z$, where X, Y, and Z are halogen atoms). A glance at the figure is sufficient to show that the part occupied by the phenyl radicle is much more closely packed than

that occupied by the SO_2Cl group. The space-ratio is about 0·60 for the phenyl group, 0·57 for the whole molecule, and 0·41 for the SO_2Cl group. Now the assemblage has been designed so that the lengths x and y shown in the diagram, and a length z denoting the height of the molecule, are compatible with three lengths which are indirectly derived from crystal measurements. The question that now arises is: What will happen when the attractive force effects a squeezing out of the interstitial space? Will the SO_2Cl end of the molecule crumple owing to a flattening of the loosely packed atoms, and so disproportionately reduce the x dimension? It will be observed that at this point we lose

FIG. 3.



all dimensional precision, and a comparison of the three values x, y, and z of the assemblage of spheres with the axial ratios of the crystal, becomes devoid of any quantitative meaning.

Equivalence Parameters.

The axial ratios $a : b : c$ of a crystalline substance are generally expressed in the form in which b is arbitrarily taken as unity; they denote the relative edge-lengths of the parallelepipedal cells, or units of the space lattice, from which the crystal may be theoretically constructed. Now the unit length b must presumably have a specific linear value for each substance, and it follows that, even in those cases in which two substances may be taken to possess similar structure, it is nevertheless inadmissible

to make any numerical comparison between the values a and a', b and b', and c and c'. With a view to bringing the units b and b' into a comparable form, Becke proposed to make use of the molecular volumes by supposing that the structural cell has the lengths of its edges in the ratios $a : b : c$, and a volume equal to the molecular volume, V, whereby it is possible to calculate a new set of ratios, $\chi : \psi : \omega$, which from their mode of origin must necessarily be the same ratios as those of the original crystal axes. The quantities χ, ψ, ω are known as "topic axes." Now, although we are as far as ever from knowing the absolute dimensions of the structural cell of either of two substances compared, we are in a position to discover the relation between the dimensions of one in terms of the other; and it is legitimate to compare χ with χ', ψ with ψ', and ω with ω'.

If, instead of the molecular volumes of two substances, we substitute the valency volume, W (that is, the total sum of the valencies in the chemical molecule where C=4, N=3, O=S=2, H=Cl=1, etc.), the equivalence parameters of Barlow and Pope are obtained. They are conveniently designated by the symbol $x : y : z$, and are similar to topic axes in so far as their ratios are identical with the original axial ratios from which they were derived. Beyond this point, however, there is, in reality, no further analogy, on account of the fundamental difference that separates the two conceptions of molecular and valency volume. The valency volumes of benzene and all its substituted halogen derivatives have *ex hypothesi* the same value, thirty, since the valency volume simply means the sum of the valencies in the molecule. The molecular volume, on the other hand, is distinctive for each substance; the molecular volume of benzene is 77·4, that of tetrabromobenzene 130·2, and so on. In view of this essential difference, Barlow and Pope have to assume that the replacement of four hydrogen atoms by four bromine atoms is accompanied by an expansion of each atom in the molecule to an extent measured by the ratio 77·4 : 130·2. Now, topic axes reflect this undoubted expansion of the molecular unit, but equivalence parameters are wholly uninfluenced by it, and as a result have no more value for the comparison of one substance with another than the original axial ratios. The failure to recognise this very real limitation of equivalence parameters has led the adherents of the theory to undertake an immense amount of computative work which has absolutely no significance. Thus, a large proportion of the evidence which has been cited in favour of the valency-volume theory consists of the following kind of "verifications": the equivalence parameters $x : y : z$, $x' : y' : z'$, etc., of a series of sub-

stances are calculated, and an approximate constancy of one of the parameters, say z,z', etc., is then held to prove that the whole series of derivatives has a structural dimension in common. For example, the theoretical part of the following memoirs—Jerusalem and Pope (*Proc. Roy. Soc.*, 1908, [*A*], **80**, 557), Jerusalem (T., 1909, **95**, 1275), Armstrong, Colgate and Rodd (*loc. cit.*)—almost wholly consists of the "proofs" that all benzene derivatives are characterised by the structural persistence of the z-parameter of benzene, namely, 2·780. In principle, such "proofs" are entirely fallacious; in actuality, they approximate to the truth (provided that truly equivalent directions in the crystals have been chosen for comparison) in those cases where the valency volumes are approximately proportional to the molecular volumes. In cases where this proportionality happens to be very close, it is obvious that equivalence parameters and topic axes become of equal significance, for $\chi : \psi : \omega$ become $kx : ky : kz$, where $k = \sqrt[3]{V/W}$.

The desirability, if not the necessity, of proving the proportionality was realised by Jerusalem (*loc. cit.*), who found in his study of picryl derivatives that it exists within the limits ±4 per cent. The smallness of these limits no doubt arises from the general similarity of the composition of the substances. It is only necessary, however, to quote the values of V/W for benzene and tetrabromobenzene, namely, 2·58 and 4·34 respectively, and again, the values for potassium, rubidium, cæsium, and ammonium sulphates, namely, 5·4, 6·1, 7·0, and 3·1, to show that the deviations from constancy of V/W can attain such an extent as entirely to discredit the kind of verification under discussion. With regard to Jerusalem's contention that the constancy of V/W within ±4 per cent. in the picryl derivatives provides a confirmation of the law of valency volumes, it is only necessary to point out that these limits are not transgressed if carbon is taken to have twice, instead of four times, the volume of hydrogen.

It is much to be regretted that the adherents of the valency-volume theory do not make a practice of determining the densities of the new substances which they subject to goniometrical measurement; not only is the density likely to acquire more and more theoretical significance, but it is also frequently of great value for purposes of identification. The molecular volumes of most of the benzene derivatives being unknown, it is impossible to test how far the proportionality V/W is constant, and hence to estimate how far the observed approximation of the z-parameters has any demonstrative value.

In order to avoid the possibility of any misapprehension, it will be well to emphasise the fact that any employment of equivalence

parameters must be carefully restricted to their ratios; thus, it is legitimate to compare, say, the ratio $x : y$ with the ratio $x' : y'$, and so on. Inasmuch as mere ratios are equally well given by the original axial ratios $a : b : c$ (and, it must be added, much more conveniently, since b is put equal to unity), it is difficult to see what benefit accrues from the calculation of the Barlow-Pope constants.

Purely Arithmetical Verifications of the Valency Volume Theory.

It is not the object of this part of the present paper to discuss the initial selections of axial ratios made by the Barlow-Pope school, but to throw into relief the practice of subsequently modifying these ratios by a process which, in the main, is entirely arithmetical. This procedure, which is generally termed a "method of treatment," was introduced by Barlow and Pope in their first memoir (*loc. cit.*, 1682), when they divided the c-axis of pentabromoethane by five. The justification for the device is presented with considerable ingenuity; essentially it consists of a general appeal to the law of rational intercepts.

The salient feature of the authors' justification is their complete failure to discriminate between the two processes of (1) an initial selection of the axial ratios by the choice of a suitable parametral face among those present, and (2) the subsequent "treatment" or modification by the multiplication of these ratios by arbitrary small numbers or fractions. The writer must insist on the necessity of a completely separate treatment of these two processes, for the ambiguity in the initial selection is primarily occasioned by a wealth of facts, namely, an embarrassing number of faces, whereas the subsequent treatment is not merely subjective and guided by preconceived requirements, but, as actually carried out, amounts to the negation of facts, inasmuch as the process involves the rejection of observed in favour of hypothetical faces.

With regard to this arbitrary arithmetical manipulation, the authors' only plea is that their illustrations demand it. This is also clearly stated by Jerusalem (T., 1910, **97**, 2194), who writes: "the use of the factor five in the multiplication of the ratio c/a is naturally justified by the very close similarity which the equivalence parameters of the three above substances exhibit after the multiplication has been performed in the case of tribenzylmethyl chloride."

That the authors are really aware of the injudiciousness of a widespread use of arithmetical methods is betrayed by the regularity with which they point out the legitimacy of appropriate modifications where these are warranted by the appearance of faces

that would permit an initial statement of the axial ratios in the form required by their theory. Thus, in discussing dibromoacetamide (T., 1910, **97**, 2311), Barlow and Pope make such an alteration in the constants as involves the allocation of the indices (101) to the face (203), and add, "the change of indices here made is legitimate, because the form (203) is actually observed." Moreover, the anxiety of the same authors to justify drastic alterations is easily apparent from certain passages, which appear to the present author to be quite irrelevant; thus on p. 2347 of the same memoir we read: "On multiplying the length by four, *the number of carbon atoms in the chain*" (present author's italics); and again, on p. 2360: "In this description it is convenient to change the indices 001, $\bar{1}01$, $\bar{2}01$, $\bar{1}11$, and 100 to 100, 203, 001, 263, and $\bar{2}03$ respectively; *the introduction of the factor three in this connection seems permissible in view of the pronounced pseudohexagonal character of the compound*, and as a result of the change the indices become more symmetrically distributed although numerically more complicated."

In conclusion, it may well be stated that the authors never seem to take into account the effect of the final "treatment" on the complexity of the indices. For example, in the first published memoir (*loc. cit.*, 1698) we read: "These axial ratios are simplified by changing the forms 100, 001, $10\bar{2}$, and $11\bar{1}$ to $\bar{1}01$, 100, 101, and 011." They fail, however, to mention that, on subsequently selecting $2a$ and $5b$, the indices finally attain the extravagant form $\bar{2}01$, 100, 201, and 051.

The Extensive Possibilities of the Arithmetical Methods of Treatment Sanctioned by the Barlow-Pope School.

The ratios between the lengths of the axes A, B, C of a crystal are ordinarily expressed in the form $a:b:c=p:1:q$, the length of the B-axis being conventionally taken as unity. Two independent constants are here involved, namely, $a/b=p$ and $c/b=q$. According to Barlow and Pope, these constants may be replaced by $h/k\,.\,p$ and $m/n\,.\,q$, where h, k, m, n denote any of the numbers 1, 2, 3, 4, or 5. Now suppose we have a "standard" rhombic substance like benzene, having the axial ratios $a:b:c=p:1:q$, with which we wish to compare any other substance—no matter whether it be a benzene derivative or a mineral like barytes. If the crystalline form presented by the latter substance is simply a combination of {110} and {101}, we can obtain one, and only one, set of axial ratios $a:b:c=p':1:q'$, and we will suppose that p' and q' present no numerical similarity to p and q of benzene. Since we are wholly in the dark as to which of the three axes

A', B', C' (if any) corresponds structurally with A of benzene, and which to B and C respectively, it is permissible to restate $p' : 1 : q'$ in five other forms, for there are six possible ways in which the two crystals may be set up so that their axes are parallel, namely, those in which $A'B'C'$, $A'C'B'$, $B'C'A'$, $B'A'C$, $C'A'B'$, $C'B'A'$ are parallel to A, B, C respectively. It is, however, extremely unlikely that any of the corresponding sets of actual ratios should present a numerical approximation to $p : 1 : q$ of benzene.

Now, if we are permitted to modify the original ratios $p' : 1 : q'$ by the employment of the multiples $h/k \times p'$ and $m/n \times q'$, limiting ourselves to the numbers 1—5 sanctioned by the Barlow-Pope usage, we shall obtain no fewer than 361 sets of revised axial ratios, each of which can be stated in six forms, so that we have altogether available 2166 different sets of the original axial ratios which can be compared with the standard values $p : 1 : q$ of benzene. By the introduction of the conception of the valency volume, a corresponding number of sets of equivalence parameters follows quite naturally. It is, however, extremely improbable that any of the 2166 variants of the axial ratios of barytes should present an absolute numerical coincidence to, say, three decimal places with the values $p : 1 : q$ of the standard substance. Some latitude must always be allowed. The adherents of the theory take as a satisfactory proof of similarity of structure any correspondence between the limits ±4 per cent. of the values for the standard substance. Most crystallographers will grant such a degree of latitude, inasmuch as the axial ratios of isomorphous substances of the rhombic system, concerning the structural resemblance of which there can be no doubt, frequently exhibit numerical differences reaching 4 per cent., and in less symmetrical systems like the monoclinic or triclinic the differences may attain even higher values.

The only question that now remains is this: No matter what are the original values of the axial ratios, are the number of variants given above (2166) sufficient to ensure that one of them, at any rate, shall present numerical values which agree with the axial ratios of the standard substance (say, benzene) within the limits of 4 per cent.? As a result of his practical examination, the writer can state that, not only is the answer in the affirmative, but there are, as a rule, several distinct ways in which the numerical resemblances can be manufactured.

As an example of the kind of results obtained by the systematic trial of the fractional multipliers allowed by Barlow and Pope, we shall for the present content ourselves with a case in which, presumably, no real resemblance can subsist, namely, barytes, $BaSO_4$,

and benzene, C_6H_6. It is seen from the table that the second and third selections lead to a very close correspondence.

Table Illustrating the Various Possibilities of a Numerical Correspondence between Barytes and Benzene.

			Deviations from benzene.	
			$a:b$	$c:b$
Barytes:	$a:b:c$	0·7622 : 1 : 1·2416		
	$3c/4:b:a$	0·931 : 1 : 0·762	+4%	−4%
	$2b/3:a:c/2$	0·875 : 1 : 0·814	−2%	+2%
	$3a/2:c:b$	0·921 : 1 : 0·805	+3%	+1%
Benzene:	$a:b:c$	0·891 : 1 : 0·799		

We may now consider systems other than the rhombic. The proportion of the comparative work of the Barlow-Pope school which refers to substances crystallised in the tetragonal, hexagonal, and rhombohedral systems is relatively small (compare p. 770), and, moreover, is not marred, to any extent, by arithmetical modifications. These systems need not, therefore, be discussed at present; the only systems remaining to be considered here are the monoclinic and triclinic.

In view of the frequent comparisons of monoclinic with rhombic substances, the authors are generally careful to choose the axial directions in such a way as to bring the monoclinic angle β as close as possible to 90°.* The subsequent procedure is then generally analogous to that adopted in comparisons of rhombic substances *inter se*, and there are, of course, just the same number of ways, namely, 2166, available for comparison with a standard substance.

As regards the comparison of the monoclinic substances *inter se*, there arrives an obvious limitation (at any rate in structurally similar compounds), owing to the need for retaining congruence of the symmetry axis. This reduces the number of available sets of axial ratios to one-third its former value, namely, 722—a number which is generally sufficient, although the deviation of the best solution from the standard may apparently rise to ±6 per cent.

* A notable exception to this rule is furnished by the morphotropic comparison made by Glover and Lowry (T., 1912, **101**, 1902) between camphorcarboxylamide and the ketonic form of benzoylcamphor, the results of which are held by the authors to furnish some evidence of the fertility of the Barlow—Pope hypothesis. The amide is brought into comparison in a form in which $\beta = 61°2'$, whilst in the rhombic benzoylcamphor $\beta = 90°$. The evidence of isomorphism is, however, altogether against any assumption that one pair of structural planes inclined at 61°2′ can in any sense correspond with another pair which are mutually perpendicular; for experience proves that an overstepping of the limit 6—7° is incompatible with isomorphism.

Substances belonging to the triclinic system have only been used to a small extent, and their employment for illustrative purposes is almost wholly restricted to the paper in which the valency volume theory was originally enunciated. In the recent work published by Armstrong, Colgate and Rodd, the general practice is to avoid triclinic substances, on the ground that no symmetry directions are available for purposes of orientation. It may, however, be observed that the same lack of precision attaches to two out of the three fundamental structural directions of the immense number of monoclinic substances which these authors have not hesitated to interpret.

A Typical Example of the Kind of Results Obtainable by the Employment of the Arithmetical Method of Treatment.

The preceding examination of the arithmetical method will have perhaps served to bring home the general conviction that any desired numerical coincidence can be effected between any substances whatsoever under comparison. It is perhaps advisable to lend force to this general impression by advancing a concrete case involving a series of compounds. Amongst the numerous illustrations which have been completely worked out by the author, a selection has been made of the following example, the choice being guided, first, by reason of space—the example is comparatively brief—and, secondly, because it can be made to furnish a proof that each and every substituent group has a valency volume one.

The axial ratios of the seven benzene derivatives enumerated in the following table are taken directly from Armstrong, Colgate and Rodd's fifth paper on benzene derivatives (*loc. cit.*, 130). This material was collected and worked out by the authors simply with the view of proving the persistence of the z-parameter of benzene throughout the series. In order to accomplish this, the process of arithmetical modification had to be applied to five out of seven members; for example, $5a/4$ was selected in the case of the parent substance trinitrobenzene, whereby the modified axial ratios became $a : b : c = 1{\cdot}1925 : 1 : 0{\cdot}7330$. The present author accepts this value of $5a/4$ merely for purposes of argument, since it really does not matter whether $5a/4$ be selected or not, and ventures to complete the table in the way indicated with the view of showing the number of ways in which any desired result may be obtained. It is seen that several alternative, fairly close solutions are possible in most cases.

It may be now stated that it is only by the employment of such arithmetical methods that Barlow and Pope have been able to adduce any crystallographic evidence in support of one of the most

Table of Arithmetically Derived Crystallographic Constants.

No.	Substance.	$a : b : c$	β.	Fractions used.	Modified ratios.
1	1 : 3 : 5-Trinitrobenzene	0·9540 : 1 : 0·7330	90°0′	$5a/4 : b : c$	1·1925 : 1 : 0·7330
2	1-Chloro-2 : 4 : 6-trinitrobenzene	1·7875 : 1 : 1·2175	90°4′	$c : b : 2a/5$	1·2175 : 1 : 0·7150
				$5c/3 : a : 4b/3$	1·1352 : 1 : 0·7459
				$3b/2 : c : a/2$	1·2320 : 1 : 0·7347
3	Picramide	0·838 : 1 : 0·6638	80°11′	$3c/2 : a : 3b/5$	1·1882 : 1 : 0·7160
				$4b/5 : c : 3a/5$	1·2052 : 1 : 0·7665
4	2 : 4 : 6:-Trinitrotoluene	0·9373 : 1 : 0·6724	90°0′	$4b/5 : c : a/2$	1·1898 : 1 : 0·6970
5	2 : 4 : 6-Trinitrobenzoic acid	1·7497 : 1 : 1·5346	90°0′	$4c/3 : a : 5b/4$	1·1694 : 1 : 0·7160
				$2a/3 : b : c/2$	1·1665 : 1 : 0·7673
				$2b : a : 4c/5$	1·1430 : 1 : 0·7000
6	2 : 4 : 6-Trinitroanisole	1·7225 : 1 : 1·4635	91°59′	$4c/3 : a : 5b/4$	1·1328 : 1 : 0·7257
				$2a/3 : b : c/2$	1·1483 : 1 : 0·7317
7	Nitromesitylene	0·5600 : 1 : 0·4878	90°0′	$5c/2 : b : 4a/3$	1·2195 : 1 : 0·7467
				$4c/3 : a : 2b/5$	1·1614 : 1 : 0·7413
				$2b/3 : a : 4c/5$	1·1905 : 1 : 0·6968
				$3b/5 : c : 2a/3$	1·2300 : 1 : 0·7653

important requirements of their theory, namely, that hydrogen has the same volume as the halogens. The method adopted is as follows. The authors regard the frequent isomorphous replacement of equivalent elements, for example, potassium, rubidium, and cæsium, or, again, chlorine, bromine, and iodine, as an indication of their volume equivalence. The crystallographic effects of a replacement of hydrogen by halogen are, however, by no means so simple; the two or three cases of an isomorphous substitution cited by Barlow and Pope (T., 1910, **97**, 2311) are clearly due to the swamping effect of a massive nucleus. Amongst comparatively simple compounds, not even a single case can be quoted in which hydrogen is isomorphously replaced by halogen. It is perhaps on this account that the Barlow-Pope school have frequently been reduced to the production of a species of "arithmetical isomorphism" by the methods exemplified in the preceding table (compare, for example, T., 1906, **89**, 1698).

It may now be pointed out that such a table of arithmetical constants can with equal force be used to indicate most diverse conclusions. Thus, although the isomorphous correspondence of the amended axial ratios of the second compound with those of trinitrobenzene may be held to indicate a volume equivalence of hydrogen and chlorine, the table equally demands that the groups NH_2, CH_3, CO_2H, and OMe shall also have unit valency volumes, whilst according to the theory their respective volumes should be 5, 7, 9 and 9. Again, if it once be granted that the methyl group and the hydrogen atom have indeed unit volumes, the inference must be drawn that the carbon atom has a negative volume of two units, and the application of this result to the isolated compound $C_6H_2Me_3 \cdot NO_2$ shows that a valency volume of seven for the group NO_2 is only compatible with a zero volume for the whole molecule. Several other equally absurd conclusions are possible, but the subject need scarcely be pursued further.

Collateral Evidence from the Chondrodite Series.

In addition to a considerable number of cases which are worked out with some stereochemical detail in terms of the appropriate sphere assemblages, the authors seek to substantiate the truth of their theory by bringing forward a mass of confirmative evidence. Much of this is of very doubtful cogency, but there are certain points which at first sight appear to be strongly in favour of the theory, and are considered by the authors to be convincing. As an example of this type of evidence, the authors have frequently drawn attention, in lectures and memoirs of a general character, to the remarkable numerical relationships existing between the

minerals of the chondrodite series and also between a certain pair of camphor derivatives.

The chondrodite series comprises the three moderately well-investigated minerals chondrodite, humite and clinohumite, the rare mineral prolectite, and also forsterite (a variety of olivine). The first three members are characterised by an extraordinarily rich facial development, and their axial ratios, as generally quoted in treatises on mineralogy, offer the following remarkable coincidences. The ratios $a:b$ are practically constant (about 1·08), whilst the values $c:b$ are approximately in the ratios 5 : 7 : 9 (namely, 3·1447 : 4·4033 : 5·6588). The mechanical interpretation of these values is that the width (b) and the depth (a) of the structural unit is relatively constant throughout the series, whilst its height (c) experiences a gradual and regular increment. Now, the composition, according to Penfield and Howe, also varies in a regular manner; the analysis of chondrodite agrees with the formula $Mg_3[2Mg(F,OH)](SiO_4)_2$, whilst humite and clinohumite contain a relatively greater amount of silica, and would appear to have the formulæ $Mg_5[2Mg(F,OH)](SiO_4)_3$ and $Mg_7[Mg(F,OH)](SiO_4)_4$. Prolectite, on the other hand, although not so fully examined, is found to have an axial ratio 1·8862, and solely on this account, for the mineral has never been analysed, it is credited with the composition $Mg[2Mg(F,OH)]SiO_4$.

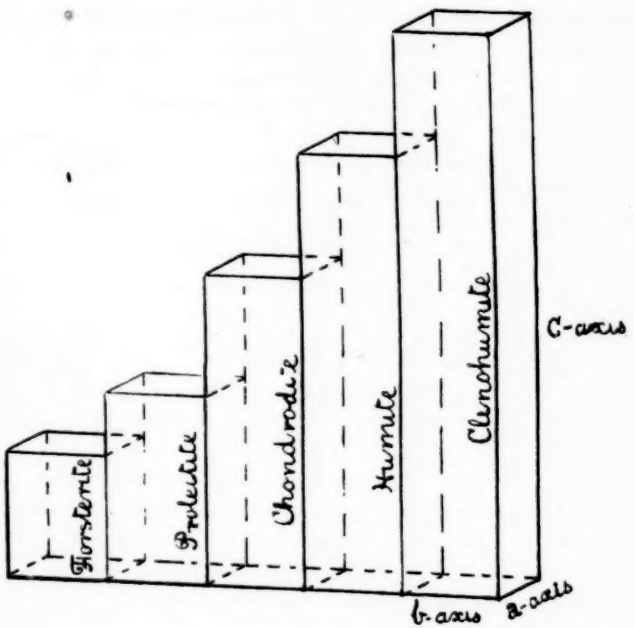
Now, it must be observed that the above four formulæ exhibit a regular increment of Mg_2SiO_4; this is the composition of forsterite, the axial ratios of which, moreover, may be stated in the form $a:b:c=1{\cdot}0757:1:1{\cdot}2601$. It is seen that forsterite has the $a:b$ ratio common to the whole series, whilst the $c:b$ ratio closely expresses the successive increments of the c-axis. All these remarkable coincidences lead to an obvious, but not by any means the only, conclusion, that the structural units of chondrodite, humite, and clinohumite are nothing more nor less than the structural unit of prolectite on which have been superimposed one, two, and three structural units of forsterite (see Fig. 4).

Granted that the above interpretation is correct, the chondrodite relation furnishes geometrical material which is eminently suited for the purpose of testing a volume theory, and the test is especially simple in the case of the valency volume theory, inasmuch as the "volume" of a compound can be obtained by the summation of the valencies of its component atoms. On subjecting their theory to the proof, in the first memoir, Barlow and Pope assume that silicon, from analogy to carbon, has a relative volume equal to four units; moreover, since the valency volume of fluorine is obviously one, and the valency volume of hydroxyl is three, the

average valency volume of the vicarious substituent (F,OH) is taken to be two. The valency volumes of the series then become: forsterite, 16; prolectite, 22; chondrodite, 38; humite, 54; clinohumite, 70. The agreement of the ratios of these values with the corresponding values of the *c*-axis is moderately good; it was held by the authors to be at least satisfactory.

In their later papers the authors are inclined to revise their assumption that silicon has a valency volume four, and propose the alternative value two, and they show that the new valency volumes are in better agreement with the crystallographic data.

FIG. 4.



It may, however, be observed that although the chondrodite series is in fair agreement with the valency volume theory, yet it is quite possible to produce a better agreement with certain other volume assumptions. A brief examination of the chemical composition on the one hand and the numerical variation of the *c*-axis on the other leads immediately to the conclusion that the correspondence between fact and theory will be closer the nearer do the hypothetical volumes satisfy the conditions: volume of Mg_2SiO_4: volume $Mg(F,OH)_2 = 2:1$. This particular condition is, of course, satisfied by an infinite number of solutions; for example,

Mg=1, Si=4, O=1, H=1; or, again, Mg=1·5, Si=4, O=2, H=1; or, again, Mg=2, Si=3, O=1, H=0·75, and so on. If, on the other hand, we select values such as Si=5, Mg=4, O=3, (F,OH)=2, we obtain $\Sigma Mg_2SiO_4 : \Sigma Mg(F,OH)_2 = 25 : 8$; and the correspondence between fact and theory is not so good, since the ratio deviates from the ratio 2:1 by an amount that is greater than the deviations resulting from the use of Barlow and Pope's valency values, these ratios being 16:6 or 14:6, accordingly as Si=4 or 2. In order to illustrate this point numerically, it is not necessary to calculate any equivalence parameters; all that is required is to show the kind of agreement obtained between the observed axial ratios of forsterite and the values they would obtain when calculated from the chondrodite series under the various assumptions.

Table of Axial Ratios of Forsterite.

	$a : b : c$
Observed values	1·0757 : 1 : 1·2601
Each and every solution satisfying $\Sigma Mg_2SiO_4 : \Sigma Mg(F,OH)_2 = 2 : 1$	1·0818 : 1 : 1·2623
Barlow and Pope's revised solution (Si=2), $\Sigma Mg_2SiO_4 : \Sigma Mg(F,OH)_2 = 7 : 3$	1·0823 : 1 : 1·2775
Any solution satisfying $\Sigma Mg_2SiO_4 : \Sigma Mg(F,OH)_2 = 25 : 8$	1·0823 : 1 : 1·2861

The above numbers show that there is very little to choose between the various values of the ratios $a : b$; with regard to the ratios $b : c$, however, the solutions $\Sigma : \Sigma = 2 : 1$ has a striking advantage over the remainder. It must now be stated that the present author is not satisfied with any of the solutions, and for the following reasons. To begin with, any ideas which merely involve a simple superposition of molecular units are scarcely in accordance with chemical experience. In the second place, the numerical coincidences involved in the axial ratios occupy a unique position in crystallographic literature, and therefore make unusual demands on one's credulity.

The view adopted by Barlow and Pope is founded on the authoritative analytical work and views of Penfield; it is, nevertheless, contrary to the spirit of the usual mineralogical method of interpretation. Chemically considered, the chondrodite group is a series of impure forsterites which contain a small and varying amount of $Mg(F,OH)_2$. When arranged in accordance with the chemical composition, the order is not that of the accepted axial ratios, namely, forsterite, prolectite, chondrodite, humite, clinohumite, but forsterite, clinohumite, humite, chondrodite, and prolectite, in which clinohumite is not far from being forsterite, pure and simple. It will be noticed that the variation in chemical

composition is not extensive; even the real end-member prolectite, $Mg[2Mg(F,OH)]SiO_4$, only differs from forsterite, Mg_2SiO_4, by the amount $Mg(F,OH)_2$. It is not without significance that the copious form development of the various minerals includes in every case a face which would allow of a restatement of the ratios in such a way as to make them all identical, and this lends support to the view that the group is a series of "varieties" of forsterite containing variable amounts of $Mg(F,OH)_2$. It must be stated, however, that this view can only be regarded as tentative, on account of: (1) the immense number of forms developed on the minerals; (2) the impossibility of rejecting many of the forms owing to statistical deficiencies in the crystallographic literature relating to the group; (3) the prevalence of macroscopic twinning; and (4) the probability that humite, being rhombic and not monoclinic, is also twinned sub-microscopically; on account of all these complexities it is impossible to subject the matter to the test of the Bravais principle (p. 767). It seems to the author that the only conclusive way of investigating the chondrodite group would be to study the thermal behaviour of fused mixtures of forsterite and magnesium fluoride, with a view to the discovery of discontinuities pointing to the formation of "double salts" of magnesium silicate and fluoride corresponding with the mineral species.

The only other example of the chondrodite type which is constantly quoted by the authors is a certain pair of camphor derivatives, namely, *d*-camphoric anhydride and the compound which camphoric acid forms with "half a molecule" of acetone. The axial ratios $b:c$ are practically identical, whilst the ratios $a:b$ stand approximately in the ratio of the valency volumes. It might at first be held that the selection of this particular case is unfortunate in view of the fact that half a molecule has no separate existence. This difficulty is, however, surmountable, for the forms developed on the anhydride will allow a "legitimate" halving of the ratio $a:b$, and the morphotropic resemblances required by the Barlow-Pope theory may be obtained in terms of the true molecular weights. Now it must be mentioned that the morphotropic resemblance, as originally pointed out by Barlow and Pope, was only obtained by doubling the ratio $c:b$ of the acetone compound, and this doubling was also conventionally permissible in view of its form development. The pair of camphor derivatives, then, is an excellent illustration of the variety of ways in which morphotropic resemblance can be "legitimately" obtained whenever a crystal exhibits a considerable number of faces. It is obvious that the existence of such ambiguities lowers the objective value of the particular morphotropic resemblance selected.

The Need of Critical Methods in the Examination of the Valency Volume Theory.

The application of crystallographic methods and results to the more abstruse, theoretical chemical problems has always been hampered by the unhappy circumstance that goniometrical measurement does not, itself, lead to any extensive knowledge concerning the internal structure of the crystal. The complexity of the connexion between form and structure can always be cited as the chief reason for the failure, but in addition there is a subsidiary, militating factor, namely, the complexity of the form itself. The number of structural planes represented on the average crystal as faces is something like ten, and this number may rise to fifty or more on very well-developed crystals of some minerals. The number of face-planes required for the computation of the axial ratios or fundamental, geometrical, crystallographic constants is, in the most general case, four. How are the four planes to be selected for merely descriptive purposes from the large number at disposal? Again, the accepted space-lattice, or three-dimensional-grating theory of crystal structure allows the general assumption that the relative dimensions of the structural unit are presented by some set or other of axial ratios. How is the set of axial ratios which in fact corresponds with the structure to be discriminated? The authors do not appear to have paid any attention to the attainment of a satisfactory solution of these problems, but, on the contrary, have been content to interpret the geometrical evidence in every case in accordance with the requirements of their theory. It is obvious, then, that the authors have not really obtained any verification of the theory, but rather have used the theory as a basis for the correct interpretation of exceedingly ambiguous geometrical evidence. This procedure can only be justified after the theory has been proved, with a reasonable degree of precision, to be an absolute fact or law of nature.

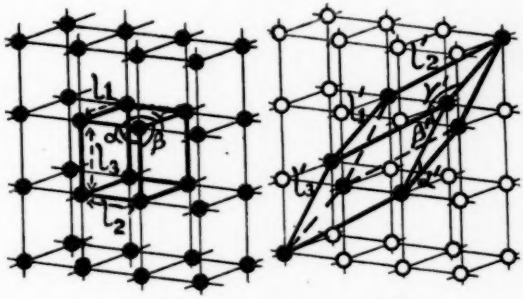
In view of the above considerations, it will, perhaps, be agreed that the valency volume theory has not hitherto been subjected by the authors to any real criticism in the light of the crystallographic facts—and this in spite of the fact that certain advances have been made during the last few years which would appear to supply an experimental basis for a critical examination of the theory.

PART III.—*Critical Methods of Correlating Geometrical Form and Crystal Structure, and their Results when Applied to the Material advanced by the Adherents of the Theory.*

The two remarkable, experimentally verified features of the geometrical development of a crystal are: (1) the constancy of angles, within very narrow limits; (2) the simple mathematical relationships connecting the various interfacial angles, and expressed in the Law of Rational Intercepts. The universally accepted space-lattice theory of crystal structure is a direct deduction from these indubitable facts.

In each crystal there subsists a precise and characteristic distribution of the units according to a space-lattice pattern. Although it is solely the relative location of these units which has

FIG. 5.



(*a*.) (*b*.)

an unambiguous meaning, it is, nevertheless, impossible to define the particular distribution without having recourse to some system or other of construction lines, as indicated in Fig. 5 (*a*). Since the assemblage is obviously a regular repetition of the cell indicated in thick lines, it follows that a statement of the relative lengths of the edges of this cell, namely, $1_1 : 1_2 : 1_3$, taken in conjunction with the values of the angles α, β, and γ between these edges, serves to define the entire assemblage of units. A glance at Fig. 5 (*b*) will, however, show that the same assemblage can be equally well defined in terms of $1'_1 : 1'_2 : 1'_3$, α', β', and γ', which refer to an entirely different set of (thick) construction lines, and it must here be mentioned that although a choice between the systems (*a*) and (*b*) (or any other systems) is of superlative importance in the province of descriptive crystallography—inasmuch as the identification of a substance by virtue of its characteristic crystalline form is impracticable unless a systematic selection be

made—the description of a space-lattice by means of any particular set of construction lines has no immediate bearing on the subject of this paper. The two questions relating to the space-lattice which, indeed, have an immediate bearing on any structure-theory can now be outlined.

The first question relates to what may conveniently be termed the "discrimination of the space-lattice," that is, the discovery of the precise and characteristic distribution of units in each individual substance. This discrimination not only entails the discovery of the space-lattice constants $1_1 : 1_2 : 1_3$, α, β, and γ in terms of some set or other of construction lines, but also a knowledge of the direction of these lines with reference to the crystal edges. It need hardly be stated that the discrimination of the space-lattices of two or more substances must always precede any serious attempt at a structural comparison of them. If this essential preliminary is neglected, there must always remain a grave suspicion that the two (or more) structures may be essentially different, however possible it may be to choose in each a set of three directions which are similar in respect of their inclinations (α, β, and γ) and the spacing of the particles along them ($1_1 : 1_2 : 1_3$). The structures, when described numerically with respect to these directions (for example, by the use of equivalence parameters), might appear to be similar, but the similarity would in all probability be illusory.

After the individual space-lattices have been ascertained, there remains a second question. There are an infinite number of ways in which an assemblage of units of the type of a space-lattice can be expressed in terms of the space-lattice constants $1_1 : 1_2 : 1_3$, α, β, and γ (two of these ways are indicated in (*b*) for the triclinic lattice of Fig. 5). A similar ambiguity holds for the lattice appropriate to a second substance. Granted that a comparison between the two substances is at all possible, it immediately follows that for each of the various modes of expression of the first lattice there exists a corresponding mode of the second lattice. It does not matter much what set of directions be chosen to determine one of the lattices provided that a corresponding set is chosen for the other. The second question, then, referred to above is: how to identify corresponding directions for comparative purposes.

We may now proceed to a brief discussion of the methods available for the solution of the two important problems outlined above.

Discrimination of the Structural Space-lattice by Means of the Bravais Principle.

An analytical method of deducing the structural space-lattice from a critical examination of the form development of a crystal was proposed by Bravais some sixty years ago, the underlying principle being the reasonable assumption that the faces of a crystal represent the most densely beset planes of the lattice. The method cannot, however, be said to have attracted much attention, partly owing, no doubt, to the labour involved in making the calculations, until it was taken up by Fedorov, who has recently shown that the calculations can be replaced by graphical methods. Since a general description of the method of employment of the Bravais principle is already available (*Ann. Reports*, 1913, 245), it need only now be stated, by way of amplification, that it is usual to estimate mathematically the "merit" of a proposed lattice (the degree of probability that it is the correct one), and then to express this merit numerically by means of a decimal fraction, which from its significance can never exceed the value 1·00. The discrimination of the real structural lattice implies the discovery of that particular lattice, the merit of which is closest to 1·00.

The following two examples will be sufficient to illustrate the general kind of results obtained when the material of the Barlow-Pope school is subjected to the test of Bravais' principle. The first example illustrates, among other things, the effect which the arithmetical process of treatment may have in degrading the merit of the space-lattice finally obtained. This feature is even more strikingly shown by the second example.

Pentabromoethane.—This substance, according to Gossner, has the following form development: $m\{110\}$, $a\{100\}$, $b\{010\}$, $q\{011\}$, $o\{\bar{1}11\}$, and, rarely, $r\{\bar{1}01\}$, the axial ratios being $a:b:c=0{\cdot}8353:1:10{\cdot}5655$, $\beta=111°5'$. The merit of the lattice in accordance with this description is found to be 0·96.

Barlow and Pope (T., 1906, **89**, 1682) first effect a transposition so as to make $a\{001\}$, $m\{012\}$, and $q\{111\}$; this gives $a:b:c=0{\cdot}5650:1:1{\cdot}5590$, $\beta=91°19'$. The merit of the lattice now involved is found to have sunk to 0·84. They then propose to divide the c-axis by five; this reduces the value of the description to 0·42. In this form the authors are able to show a "close crystallographic similarity" to hexabromoethane; the low value 0·42 is, however, a sufficient proof that the close crystallographic similarity is not due to any real structural resemblance.

In the subsequent paper, in which the authors develop the

configuration of the ethane derivatives (T., 1910, **96**, 2335), it is found "to be convenient to double the ratios of $c:b$" for the penta- and hexa-bromoethanes. The merit of the space-lattice for pentabromoethane now rises to 0·48. The configuration suggested by the authors for ethane is found by them to be in agreement with the crystallographic description, as interpreted in the light of this space-lattice. As far as the Bravais principle has any value for the determination of the structure of a crystal from its form, the present author concludes, on the contrary, that the crystallographic confirmation supplied by the authors has a vanishingly small value, for this reason: for a crystal of a given form development the number of alternative space-lattices having a merit 0·40 is usually so great that one of them can always be found which shall agree with any preconceived structure whatsoever.

Benzenesulphonyl-o-toluidide.—This substance was measured by Armstrong, Colgate, and Rodd (*loc. cit.*, 162), who found the faces developed to be {010}, {011}, {110}, and {210}, the calculated axial ratios being $a:b:c=0{\cdot}7780:1:0{\cdot}5910$. The merit of the space-lattice corresponding with these ratios is found by the writer to be 0·78.

In order to bring about an agreement between the suggested molecular configuration and the crystallographic constants, the authors proceed to select $3a$ and $4c/3$. Now, it will be observed that the possible form {100}, normal to the lengthened a-axis, is not represented in the form development. It can therefore be predicted that the particular arithmetical modification advocated should have a very grave effect on the merit of the space-lattice; as a matter of fact, the value sinks to 0·22. Since an average crystalline substance can be described in terms of some hundreds, if not thousands, of different space-lattices, each with a merit above 0·22, the writer cannot accept the authors' optimistic view that they "seem to have arrived at a satisfactory solution of the structure of the *o*-toluidide." *

The Problem of the Discovery of Corresponding Directions.

The general solution of this problem can never be reached by the application of geometrical methods alone; such methods must be supplemented by experimental work. One of the most suitable

* It may be mentioned that the diagram appended by the authors is distinguished by the presence of certain large cavities, which are so flattened as to withstand the intrusion of the smallest size sphere used (that is, a hydrogen atom); the volume of the cavity is, nevertheless, some two units greater than the volumes of other cavities in the structure, which in these circumstances can hardly be described as "close-packed."

methods of exploring crystal structure is that adopted by the writer some ten years ago, at the suggestion of Sir (then Prof.) H. A. Miers. This method depends on the investigation of the effect of a crystal on the orientation taken up by crystals of another substance when deposited on its surface from solution (T., 1906, **89**, 1120). In addition to this method, recourse may also be had to the evidence afforded by cleavage directions. Since, however, the adherents of the valency volume theory do not, in general, appeal to physical methods, we must briefly discuss to what extent the symmetry of a crystal may render assistance.

Of the three kinds of symmetry which are consistent with a space-lattice structure *per se*, namely, centre, plane, and axis of symmetry, the universal subsistence of the first element mentioned follows from the equal spacing of the particles along every structural line; its presence in the triclinic lattice of Fig. 5 is of no assistance in the discrimination of corresponding directions for comparative purposes. The addition of a two-, three-, four-, or six-fold axis of symmetry endows the resulting monoclinic, rhombohedral, tetragonal, and hexagonal lattices with a unique direction, which is of great value as an aid to orientation. It must, however, be remembered that comparisons have to be effected in terms of ratios involving a knowledge of two comparable directions. Now, the combination of a centre with an axis of symmetry always involves additional symmetry in a lattice. This additional symmetry gives no further help to orientation in the monoclinic lattice. The case is, however, quite different with the rhombohedral, tetragonal, and hexagonal lattices; but there still remains an ambiguity, for alternative selections are still possible in the matter of subordinate, structural directions. In the two remaining types of lattice—the rhombic and the cubic—there is no longer any unique direction; its absence is, however, only felt in the former system, for in the cubic system the lattice constants are completely determined by the symmetry; in the rhombic system, on the other hand, the only compensation is a fixity of the three principal directions.

The general subject of partial geometrical solutions, or, conversely, partial degrees of freedom, is of considerable importance in any critical examination of the valency volume theory, for it enables an approximate estimate to be made as to how far any general correspondence between fact and theory is due to the number of degrees of freedom necessarily allowed in a purely geometrical interpretation of the crystallographic evidence. It is to be expected that the greater the number of ways in which the

geometrical evidence may be legitimately treated, the easier will be the obtainment of an apparently satisfactory mechanical solution. Is it merely a coincidence that the relatively successful cases, examined by Barlow and Pope, mostly belong to that system which allows of the greatest freedom of treatment, namely, the rhombic?

Detailed Examination of the more Cogent Cases presented by the Barlow-Pope School.

A detailed discussion of every individual piece of evidence published in support of the valency volume theory is obviously not practicable, and, the writer believes, is also unnecessary, since no case involving an arithmetical modification of the geometrical constants need be seriously considered—as stated previously, the result of this is to rule out something more than 90 per cent. of the material. Moreover, several other cases have already been treated in detail, as, for example, the chondrodite series. The small residue of what may be termed the more cogent cases will now be briefly considered. The list is intended to be a complete one; it is, however, quite possible that an example or two may have been inadvertently omitted.

1. *Invariant System* (*the "Cubic"*).

In the cubic system the space-lattice constants are fixed by the symmetry, and from the point of view of geometrical crystallography any molecular configuration may be considered satisfactory provided the arrangement of the molecules in the crystal is in accordance with the symmetry. Barlow and Pope's discussion of several cubic elements and binary compounds has no quantitative bearing on the valency volume theory.

2. *Divariant Systems* (*the Hexagonal, Tetragonal, Rhombohedral, and, in a Sense, the Monoclinic Systems*).

The common characteristic of these systems is the possession of a unique direction of symmetry, which is naturally assumed to be a principal structural direction. It is also usual to assume that the two remaining principal structural directions lie in the plane normal to the unique axis (in some cases three directions are reckoned, although one of these is quite superfluous). The divariancy comes about by virtue of the fact that there are two alternative selections of this pair of structural directions. The monoclinic system is only divariant provided that the choice of structural directions is dictated by the endeavour to obtain a value

of β as near as possible to 90°, although from its lower type of symmetry greater possibilities of variation might be expected.

It must be emphasised that the divariant systems are, from their nature, by far the most suitable for any attempt to test the truth of a volume theory, inasmuch as quantitative comparisons just become possible, and the flexibility of the crystallographic material is at a minimum. Anyone who adopts a sceptical attitude towards the Barlow-Pope theory would expect the number of cases successfully treated by the authors to have a low percentage value in divariant systems. It will be seen that tetragonal crystals are wholly unrepresented in the following lists of the relatively successful cases. Successful solutions for such simple compounds as cassiterite, SnO_2, and its isomorphs; mercuric iodide, HgI_2; anatase, TiO_2; zirconium dioxide, ZrO_2, would, in the writer's opinion, carry a relatively considerable weight.

		$c:a$	
Hexagonal system.—GlO	.....	1·6305	
ZnO	.....	1·6077	
ZnS	.....	0·8175	or better 1·6350
CdS	.....	0·8109	or better 1·6218
AgI	.....	0·8196	

The space-lattice adopted for the oxides and sulphides, which corresponds with the above numbers, is in agreement with the form development, and the resulting values of $c:a$ agree well with the theoretical value as calculated from the close-packed arrangement of equal spheres, namely, 1·6330 (T., 1907, **91**, 1169). Silver iodide is so variable in its external form that it is impossible to deduce the space-lattice with any certainty by the use of the Bravais principle. In the above list the five substances are given separately, although in any statistical estimate of successes and failures the members of an isomorphous group should count as one substance, for the reason that only one structure is involved. The isomorphism of the two oxides on the one hand, and of the two sulphides on the other, can scarcely be disputed. It is also possible that the oxides are isomorphous with the sulphides. If this view is accepted, the five substances represent collectively, two successes, when silver iodide is allowed to be a success.

Rhombohedral system.—Sodium nitrate, $NaNO_3$ (and calcite, $CaCO_3$).

The assemblages suggested for these isomorphous substances (T., 1908, **93**, 1538) are in agreement with the space-lattice, as discriminated by the Bravais principle.

Tetragonal system.—None.

Monoclinic system.—Carbon tetrabromide (?).

The writer is not sure that he correctly understands the initial

transformation of indices effected by the authors (T., 1910, **97**, 2323); if the authors will state the transformation equations, the case can be finally examined. At present it would appear that the real space-lattice is not the simple pseudo-cube adopted in the molecular configuration suggested, but rather the lattice obtained by centring the faces of this pseudo-cube.

3. *Hexavariant System (the Rhombic).*

This system is hexavariant, inasmuch as there are six positions in which a rhombic crystal can be compared with another rhombic crystal or model. Such positions correspond with the six aspects of the axial ratios discussed on p. 755. The following are regarded as the most cogent cases.

Benzene, C_6H_6 (T., 1906, **89**, 1692).—The correspondence between the relative dimensions of the suggested configuration and the axial ratios is quite good. It is, however, in some ways unfortunate that the authors selected benzene as a starting point instead of certain of its derivatives, since good crystals have never been obtained. It is not the numerical accuracy of the axial ratios, as given by Groth, which the writer has in view (for a difference of a unit or two in the second place of decimals would probably not affect the comparison with the Barlow-Pope configuration), but rather the uncertainty that must attach to any substance the geometrical development of which is so little known as to preclude any trustworthy knowledge of the space-lattice.

Rubidium dichlorobromide, $RbCl_2Br$, *and its isomorphs.*—This series, containing some sixteen members, has been examined by Barlow and Pope in great detail (T., 1907, **91**, 1192; *Brit. Ass. Contribution*, 1907, 9). It is of great interest, since all the elements concerned have the same valency, and according to the authors' theory the configuration is therefore simply a close-packed assemblage of equal spheres. The axial ratios range between certain limits, the mean values being $a : b : c = 0{\cdot}7081 : 1 : 1{\cdot}1435$. According to Barlow and Pope, the corresponding values of the ideal assemblage of equal spheres are $0{\cdot}6124 : 1 : 1{\cdot}0608$, and show a discrepancy amounting to 16 per cent. and 8 per cent. for the ratios $a : b$ and $c : b$ respectively. The space-lattice implied by the authors' configuration is not in accordance with the Bravais principle.*

* The authors would seem to be under the impression that the dimensions, $a : b : c = 1 : 2\sqrt{2/3} : \sqrt{3} = 0{\cdot}6124 : 1 : 1{\cdot}0608$, which can be traced in the hexagonal assemblage of equal spheres, also hold for the assemblage under consideration. This view is erroneous; the circumstances that the present assemblage contains three atoms of one element (or of one chemical type of

Ammonium tri-iodide, NH_4I_3.—This substance is of importance as being the only non-cubic ammonium salt which the authors have studied in detail. The substance is isomorphous with the members of the preceding group, and the configuration suggested by Barlow and Pope is based in the main on the configuration advocated for that series. Several diagrams are given illustrating the final configuration obtained, as well as the procedure adopted in its derivation. From these diagrams the writer estimates the values $x : y : z$ to be approximately 2·45 : 2·85 : 4·3, which give the values $a : b : c = 0·86 : 1 : 1·4$, whilst the measured crystal has the values 0·6950 : 1 : 1·1415. It must be noted that the ratio $a : c$ is correct, but the b-axis (y-parameter) of the diagram is much too short. Since the diagrams are always drawn to scale, the writer ventures to call the attention of the authors to this discrepancy with a view to its eventual elucidation.

The above general examination of the material which has been advanced in support of the valency volume theory reveals some five cases in which the authors' interpretation of the geometrical evidence may be regarded as satisfactory. Since, on the other hand, the authors have discussed at least a hundred substances, the writer cannot help drawing the conclusion that the theory has so far received no general crystallographic support.

The author has great pleasure in expressing his deep gratitude to Prof. H. L. Bowman, who very generously undertook the careful perusal of the original manuscript; any merits the paper may have in its present, abridged form are very largely due to his acute criticisms and helpful advice.

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[*Received, March 15th*, 1915.]

element—halogen) to one atom of another element introduces a modifying influence, which determines a halving of the b-axis. As a matter of fact the isomorphous series in question sometimes presents the development of the form $f\{021\}$ which conventionally will allow the requisite halving of the b-axis; the occasional appearance of this face determined the inclusion of the series in this list of cogent cases.

LXXXI.—*The Freezing-point Diagrams of Formamide with Water and the Aliphatic Acids and their Bearing on the Interpretation of Viscosity Measurements.*

By Solomon English (1851 Exhibition Scholar) and William Ernest Stephen Turner.

The interpretation of the viscosity maxima which are given by certain liquid mixtures is a matter on which physical chemists are not yet in agreement. Considerable evidence has, however, been put forward by Thole, Mussell and Dunstan (T., 1913, **103**, 1108) as the result both of their own experiments and of data acquired from other sources that such maxima are connected with the formation of a compound or compounds between the components.

The larger and, it appears to us, more important problem turns on the utility of this property as a criterion of the formation of compounds in solution. For if it is to be capable of application as an independent physical test, not only should viscosity maxima always indicate the formation of compounds, but also, conversely, the formation of a compound should always influence the viscosity curve in some definite manner, as by the production of a maximum.

On the latter question, Thole, Mussell and Dunstan indicate the possibility of cases where (owing to the initial state of association of the constituents) the components do unite to give a compound the viscosity of which is less than that of either component. An actual example, where freezing-point data indicate a compound, whereas viscosity measurements do not, is phenol-acetone (Schmidlin and Lang, *Ber.*, 1910, **43**, 2812), but the great difference in temperature at which the separate properties are measured may largely account for this discrepancy. Our paper contributes to the elucidation of this point.

The determination (Merry and Turner, T., 1914, **105**, 748) of the viscosities of mixtures of formamide with formic, acetic, propionic, and *n*-butyric acids left us in doubt as to whether or not the components united. In the cases of acetic, propionic, and *n*-butyric acids, it is true, pronounced maxima were obtained; but formic acid did not behave similarly, and there appeared to be no reason why, if the three other acids formed compounds, formic acid should not do so likewise. Therefore, in admitting the probability of the formation of compounds, we gave weight rather to external evidence (the existence of compounds of formamide with the halogen acids) than to the viscosity data.

In order, therefore, both to satisfy ourselves on the soundness of our conclusions, and also to accumulate evidence on the degree of utility of viscosity measurements, we decided to investigate the freezing-point diagrams of mixtures of formamide with formic, acetic, propionic, and *n*-butyric acids, and also with water. As already stated, three of these mixtures give viscosity maxima; formamide and formic acid give a convex curve without a maximum; formamide and water give a sagged or concave curve.

The results of the freezing-point determinations will first be presented, and their bearing on the viscosity data considered later.

The freezing-point measurements were made with a standardised pentane thermometer, the cooling medium, where ice and salt were useless, being either solid carbon dioxide and ether, or ether cooled by liquid air. As the substances under investigation are hygroscopic, a current of air, dried by sulphuric acid and phosphoric oxide, was circulated through the upper part of the freezing-point tube. Supercooling, as will be seen below, was often very pronounced. Each curve has, however, been constructed from numerous observations, and, in addition to those recorded, a large number of others were taken in confirmation.

The formamide used throughout was purified by methods already described (English and Turner, T., 1914, **105**, 1656), and the melting points of different samples varied between 2·05° and 2·20°.

Formamide–Water.

The freezing points of solutions of different strengths were:

Mols. per cent. formamide.	F. p.	Mols. per cent. formamide.	F. p.
0·00	− 0·0°	37·37	−38·9°
3·819	− 2·7	40·32	−42·5
6·670	− 5·7	42·87	−45·4
7·125	− 5·9	46·59	−40·4
11·370	− 9·9	49·10	−40·0
12·41	−11·0	51·62	−37·6
18·11	−16·8	55·54	−33·5
24·67	−23·6	59·64	−29·4
25·92	−24·3	64·03	−25·5
28·88	−27·5	68·35	−21·9
31·76	−31·1	76·98	−14·5
34·47	−34·7	87·68	− 6·40
		100·00	+ 2·20

The freezing-point curve (Fig. 1) consists of three branches, the second break from the water end corresponding with a compound $H{\cdot}CO{\cdot}NH_2,H_2O$, the stability of which is evidently limited.

Walden and Zawidzki (*Zeitsch. physikal. Chem.*, 1906, **54**, 180), from determinations of the molecular weight of formamide in water, drew the conclusion that chemical combination did not

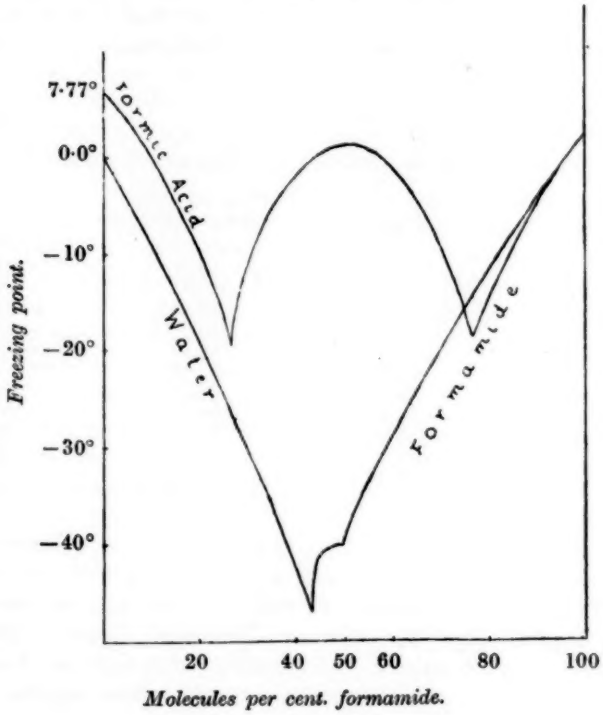
occur. This conclusion is scarcely correct, but it is probable that clear indications of the presence of the compound would not be obtained from a molecular-weight determination carried out over the accustomed limited range of concentration.

Formamide–Formic Acid.

The formic acid was purified by fractional distillation. The freezing-point data are:

Mols. per cent. formamide.	F. p.	Mols. per cent. formamide.	F. p.
0·00	7·77°	53·28	+ 1·1°
5·17	3·9	56·65	+ 0·7
11·44	− 0·9	58·86	− 0·5
20·60	−10·3	61·90	− 2·2
25·12	−16·8	65·64	− 4·9
29·00	−12·7	69·76	− 8·7
33·95	− 6·4	73·93	−14·1
35·62	− 6·0	78·56	−16·3
39·16	− 3·7	83·41	−11·4
40·51	− 1·6	90·19	− 5·0
45·87	+ 0·2	100·00	+ 2·05
50·06	+ 1·1		

FIG 1.



The curve (Fig. 1) clearly indicates the formation of a compound derived from one molecule of each constituent,

$$H{\cdot}CO{\cdot}NH_2,H{\cdot}CO_2H,$$

the melting point of which is 1·1°. The central portion of the curve is most emphatic, but the existence of the compound was confirmed by analysis. For this purpose, a mixture of nearly equivalent proportions was partly frozen, the solid rapidly filtered and removed to a porous dish in a desiccator surrounded by ice and water. Analysis of the dry material by titration with $N/10$-sodium hydroxide showed that the crystals contained 49·97 per cent. of acid; $H{\cdot}CO{\cdot}NH_2,H{\cdot}CO_2H$ requires 50·5 per cent.

Formamide–Acetic Acid.

The acetic acid, specially purified (compare Merry and Turner, *loc. cit.*), melted at 16·60°. The following numbers are a selection from the data obtained for the solutions:

Mols. per cent. formamide.	F. p.	Mols. per cent. formamide.	F. p.
0·00	16·60°	53·26	−15·3°
1·614	15·60	57·63	−18·7
4·831	13·71	62·01	−22·7
10·71	10·01	66·28	−28·2
13·85	7·82	67·48	−29·3
18·99	3·82	69·34	−27·6
25·77	− 2·41	70·84	−25·1
31·75	− 7·55	73·35	−22·3
35·67	− 8·2	77·21	−16·3
39·05	− 8·4	81·59	−11·9
42·70	− 9·4	85·06	− 9·0
46·93	−11·2	91·91	− 3·24
50·05	−12·4	96·72	+ 0·10
		100·00	+ 2·05

The mixture containing 35·67 mols. per cent. of formamide gave an initial freezing point of −12·8°, slowly rising to −8·20°; whilst the 39·05 per cent. mixture could be cooled to −21° and required seeding (a crystal of acetic acid was sufficient), and then froze at −8·42°.

The curve (Fig. 2, p. 778) indicates a maximum at nearly 33 per cent. formamide, corresponding with the compound

$$H{\cdot}CO{\cdot}NH_2,2CH_3{\cdot}CO_2H.$$

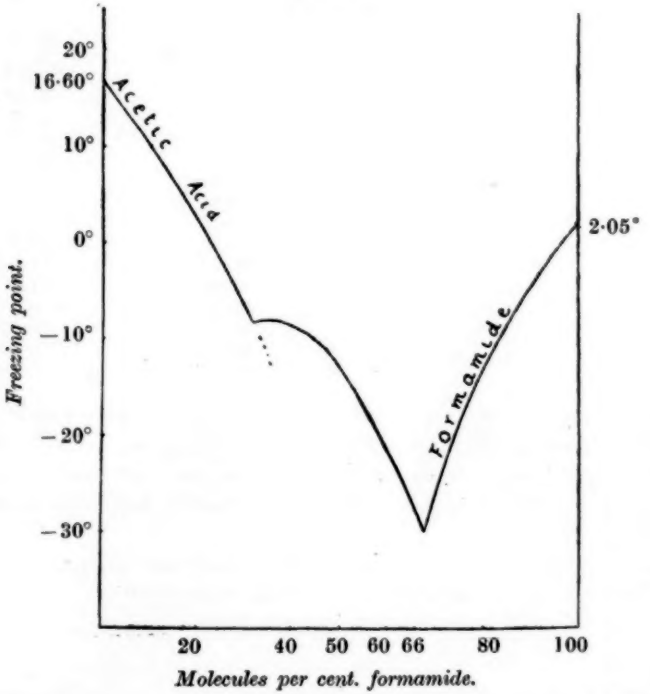
Formamide–Propionic Acid.

The acid was purified by fractional distillation until its freezing point was constant. Three portions, freezing at −20·80°, −20·85°, and −20·80°, respectively, were combined, and yielded on further fractionation a product freezing at −20·85° to −20·90°.

Freezing-point determinations were made on more than fifty solutions of different compositions, but only those essential for the curve are given:

Mols. per cent. formamide.	F. p.	Mols. per cent. formamide.	F. p.
0·00	−20·71°	57·41	−14·4°
7·025	−23·5	59·36	−13·2
11·36	−25·0	62·44	−12·3
19·22	−28·5	66·18	−11·6
27·19	−33·0	69·07	−11·2
32·25	−36·7	70·96	−12·5
37·36	−34·8	72·71	−13·9
41·25	−24·7	74·39	−16·3
44·50	−23·7	77·24	−15·4
47·36	−21·9	80·14	−12·4
49·20	−21·8	87·75	− 6·2
51·06	−20·5	91·75	− 3·02
53·75	−17·4	96·07	− 0·1
55·55	−15·6	100·00	+ 2·07

FIG. 2.



Very pronounced supercooling occurred, and the liquid was very viscous at the lower temperatures. The degree of supercooling is illustrated by the following first and final freezing points:

59·36 per cent. formamide.....	−36·5°	and −13·2°
57·41 „ „ „	−41·5	„ −14·4
55·55 „ „ „	−43·0	„ −15·6

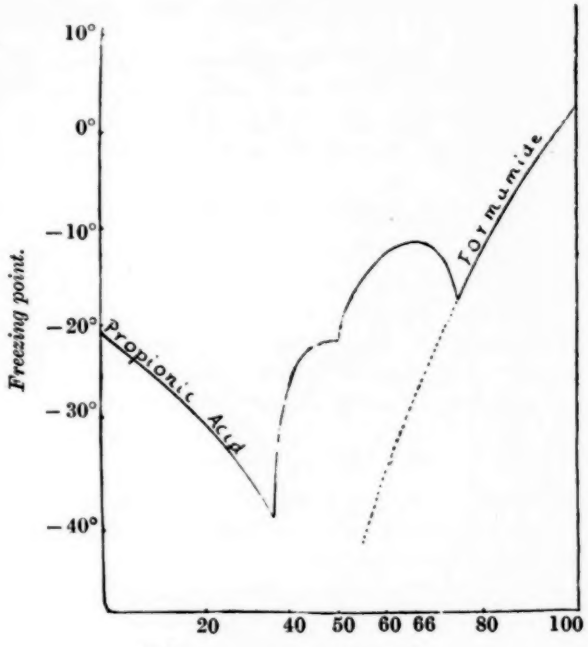
The broken portions of the curve represent quite a number of observations of first freezing points.

The curve (Fig. 3) contains two maxima, at 50 and 66 mols. per cent. formamide, corresponding, respectively, with

$H{\cdot}CO{\cdot}NH_2,C_2H_5{\cdot}CO_2H$ and $2H{\cdot}CO{\cdot}NH_2,C_2H_5{\cdot}CO_2H$,

of which the latter appears to be the more stable one.

FIG. 3.



Formamide–n-Butyric Acid.

The acid, purified in the same manner as the propionic acid, froze at −4·65° to −4·70°. The data for the solutions are:

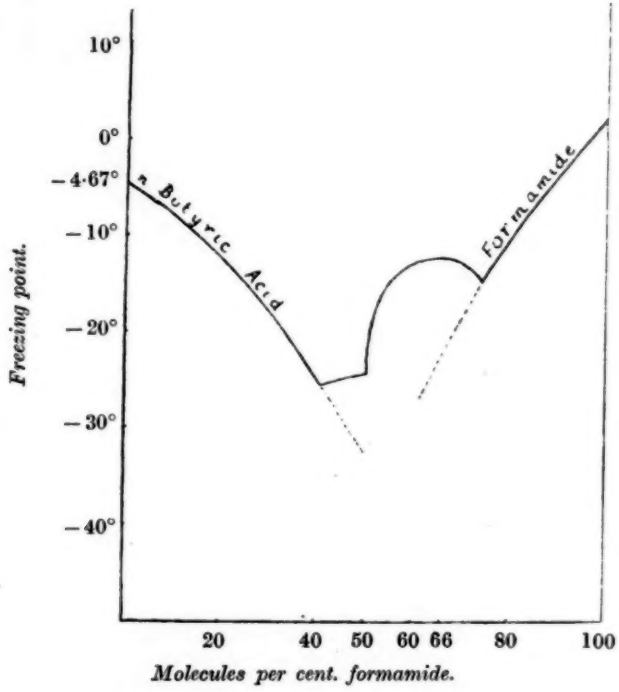
Mols. per cent. formamide.	F. p.	Mols. per cent. formamide.	F. p.
0·00	− 4·67°	61·87	−12·6°
18·45	−11·72	66·37	−12·3
27·29	−15·57	70·03	−12·9
32·83	−20·45	77·45	−11·8
41·15	−23·4	80·67	− 9·47
43·50	−24·7	84·03	− 7·82
47·37	−24·5	87·34	− 5·35
50·19	−24·3	90·95	− 3·35
51·80	−18·7	95·06	− 0·67
53·83	−16·3	98·11	+ 1·25
58·42	−13·8	100·00	+ 2·20

Additional observations are given on the broken curves indicating supercooling.

The curve (Fig. 4) consists, like that for propionic acid, of four branches. The transition point on the flattened curve corresponds with $H{\cdot}CO{\cdot}NH_2,C_3H_7{\cdot}CO_2H$, and the maximum on the third curve with $2H{\cdot}CO{\cdot}NH_2,C_3H_7{\cdot}CO_2H$.

It is thus evident that the four aliphatic acids do not form compounds of the same type with formamide. Propionic and *n*-butyric acids behave very similarly, each forming two com-

FIG. 4.



pounds. The single compound formed by acetic acid agrees with not one of the compounds derived from the three other acids. This behaviour is paralleled by that of formamide with the hydrogen haloids. Thus, we have $H{\cdot}CO{\cdot}NH_2,3HCl$ (Röhler, *Zeitsch. Elektrochem.*, 1910, **16**, 419) and $2H{\cdot}CO{\cdot}NH_2,HBr$ (Walden, *Bull. Acad. Sci., St. Pétersbourg*, 1911, p. 1055).

General Discussion of Results.

The significance of the results can be readily appreciated by contrasting them with the viscosity data previously obtained. The

portions in italics below are quotations from the summarised results of a previous paper (Merry and Turner, *loc. cit.*). By the term viscosity deviation is meant the departure from the linear relationship.

The viscosities referred to were measured at 25°.

Formamide–Water.

Viscosity.—Less than the calculated value, giving a sagged curve.

Viscosity deviation.—Maximum at 40 mols. per cent. formamide.

Freezing-point curve.—Maximum at 50 mols. per cent. of each.

A compound, $H{\cdot}CO{\cdot}NH_2,H_2O$, is formed. The conclusion drawn from the viscosity data was that no compound is formed.

Formamide–Formic Acid.

Viscosity.—Greater than calculated, but no maximum.

Viscosity deviation.—Maximum at 50 mols. per cent.

There is possibly a compound, $H{\cdot}CO{\cdot}NH_2,H{\cdot}CO_2H$.

Freezing-point curve.—Pronounced maximum at 50 mols. per cent. Undoubtedly a compound is formed from one molecule of each constituent, having a freezing point of $+1{\cdot}1°$.

Formamide–Acetic Acid.

Viscosity.—Maximum at 64—65 per cent.

Viscosity deviation.—Maximum at 50 per cent.

The evidence may indicate the formation of a compound, $H{\cdot}CO{\cdot}NH_2,CH_3{\cdot}CO_2H$, *rsembling the one with formic acid.*

Freezing-point curve.—Maximum at 33 mols. per cent. formamide.

Evidently the earlier conclusion is incorrect, and the three methods of testing the formation of compounds given above are not in harmony with one another.

Formamide–Propionic Acid.

Viscosity.—Maximum at 70 per cent.

Viscosity deviation.—Maximum at 65 per cent.

A possible compound, $2H{\cdot}CO{\cdot}NH_2,C_2H_5{\cdot}CO_2H$.

Freezing-point curve.—Two maxima, at 50 and 66 per cent.

The freezing-point data confirm the existence of the compound previously suggested, but the viscosity data obviously give no hint of the formation of the equimolecular compound.

Formamide–n-Butyric Acid.

Viscosity.—Maximum at 63 *per cent.*

Viscosity deviation.—Maximum at 65 *per cent.*

A compound of the formula $2H{\cdot}CO{\cdot}NH_2,C_3H_7{\cdot}CO_2H$ *may be present.*

Freezing-point curve.—Two compounds formed.

This case is precisely similar to that of propionic acid.

The following conclusions on the utility of viscosity measurements in testing the constitution of liquid mixtures may be drawn:

(1) Although maxima on viscosity curves may be due to chemical union between the components of the mixture, the presence of compounds is not, on the other hand, always accompanied by viscosity maxima.

It could very reasonably be urged that the compound formed between formamide and water (as with phenol and acetone) is so unstable that it exists only at low temperatures, so that at 25° it would be completely dissociated, and exercise no influence on the viscosity of the mixture. It is also possible that if the viscosity of formamide–formic acid were determined at 10° instead of 25°, a maximum might be found. However, viscosity measurements at low temperatures would, without doubt, be much more difficult to carry out than freezing-point determinations.

(2) Viscosity curves do not appear to differentiate between, or even to indicate, the existence of more than one compound in the mixture.

(3) The method of distinguishing the composition of a compound by determining the composition at which the viscosity deviates most from the calculated value (Findlay, *Zeitsch. physikal. Chem.*, 1909, **69**, 203; Denison, *Trans. Faraday Soc.*, 1912, **8**, 20) does not appear to be infallible, for the maximum deviation of the viscosity lies at 40, and not, as it should do, at 50, molecules per cent. of formamide for the mixture with water, whilst with formamide–acetic acid the maximum deviation lies at 50 mols. per cent., whereas the compound only contains 33 mols. per cent. of formamide.

We have not, it may be remarked, brought forward in this paper any evidence that viscosity maxima may be due to any cause other than the formation of compounds. In earlier papers (Merry and Turner, *loc. cit.*; English and Turner, *loc. cit.*) we have discussed this point, and we hope as the outcome of further investigation to arrive at a definite conclusion.

Some of the materials used in this investigation were purchased

by the aid of a grant kindly made by the Government Grant Committee of the Royal Society. We would also especially thank Dr. A. E. Dunstan for a specimen of formamide, and Dr. R. H. Pickard for one of *n*-butyric acid, which enabled this section of the work to be carried to completion.

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THE UNIVERSITY, SHEFFIELD. [*Received, May 3rd*, 1915.]

LXXXII.—*Syntheses with the Aid of Monochloromethyl Ether. Part III. The Action of Monochloromethyl Ether on the Sodium Derivatives of Ethyl Ethane-aββ-tricarboxylate, Ethyl Butane-aaδδ-tetracarboxylate, and Ethyl Pentane-aaεε-tetracarboxylate.*

By JOHN LIONEL SIMONSEN.

DURING the course of certain synthetical experiments, which are at present in progress, the author desired to prepare a considerable quantity of *cyclo*propane-1 : 2-dicarboxylic acid, and since the processes at present available for the preparation of this acid (Perkin and Tattersall, T., 1905, **87**, 306) are very laborious, an attempt was made to devise a new method. It was shown some time ago (Simonsen, T., 1908, **93**, 1781; Perkin and Simonsen, T., 1909, **95**, 1171) that when ethyl δ-methoxybutane-*aa*γγ-tetracarboxylate (I) was hydrolysed with hydrochloric acid, it was converted quantitatively into *cis-cyclo*butane-1 : 3-dicarboxylic acid (II), the reaction taking place in accordance with the following scheme:

$$\underset{\text{(I.)}}{OMe\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)_2} \longrightarrow \underset{\text{(II.)}}{\begin{matrix} CH(CO_2H)\cdot CH_2 \\ | \quad\quad | \\ CH_2 \text{———} CH\cdot CO_2H \end{matrix}}$$

It therefore appeared probable that *ethyl* γ-*methoxypropane-aββ-tricarboxylate* (III) might behave similarly, and yield the required *cyclo*propanedicarboxylic acid (IV):

$$\underset{\text{(III).}}{OMe\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CO_2Et} \longrightarrow \underset{\text{(IV.)}}{CH_2\begin{matrix} CH\cdot CO_2H \\ | \\ CH\cdot CO_2H \end{matrix}}$$

Ethyl γ-methoxypropane-*aββ*-tricarboxylate is readily obtained by the condensation of monochloromethyl ether with the sodium

derivative of ethyl ethane-**αββ**-tricarboxylate when the reaction is carried out under the conditions described in the experimental part of this paper (p. 786). Unfortunately, however, this ester showed no tendency to lose methyl alcohol with the formation of the cyclic compound.

On hydrolysis with hydrochloric acid, it yielded itaconic acid, and this is probably the simplest method for the preparation of this important acid. When the ester is subjected to hydrolysis with either alcoholic potassium hydroxide or barium hydroxide, *γ-methoxypropane-αββ-tricarboxylic acid* is obtained, which melts at 146°, with loss of carbon dioxide and formation of *γ-methoxypropane-αβ-dicarboxylic acid*. That this acid has the constitution assigned to it is shown by the fact that on treatment with hydrogen bromide it yields γ-bromopropanedicarboxylic acid, and with hydriodic acid the corresponding iodo-acid. When γ-methoxypropane-**αβ**-dicarboxylic acid is distilled under ordinary pressure it loses water and methyl alcohol, yielding the anhydride of citraconic acid, whilst when it is treated with acetyl chloride an oil is obtained, which crystallises on the addition of water, and evidently consists of the anhydride of γ-chloropropane-**αβ**-dicarboxylic acid, since this acid is found to be the sole product of the reaction. The formation of the halogen acid is somewhat remarkable in view of the fact that Anschütz (*Ber.*, 1880, **13**, 1539) made use of this reagent for the preparation of the anhydride of unsaturated acids.

Since it has been shown by Perkin and Tattersall (*loc. cit.*) that the sole product of the action of alcoholic potassium hydroxide on ethyl bromoglutarate was *cis-cyclo*propane-1 : 3-dicarboxylic acid, it appeared probable that γ-bromopropane-**αβ**-dicarboxylic acid might behave similarly and yield the cyclic acid. The action of alcoholic potassium hydroxide on the bromo-acid was therefore carefully investigated, but it was found that the product of the reaction in this case was the unsaturated acid, mesaconic acid.

It is perhaps of interest to note that ethyl γ-methoxypropane-**αββ**-tricarboxylate can, under suitable conditions, be made to yield the three isomeric acids, itaconic, citraconic, and mesaconic acids.

Since ethyl γ-methoxypropane-**αββ**-tricarboxylate did not yield the expected cyclic acid on hydrolysis, it appeared possible that the formation of the unsaturated acid might be due to the fact that *cyclo*propane derivatives are generally somewhat unstable. It was therefore decided to attempt the preparation of esters which should, on hydrolysis, yield *cyclo*pentane and *cyclo*hexane derivatives.

For this purpose, the condensation of monochloromethyl ether with the sodium derivatives of ethyl butane-**ααδδ**-tetracarboxylate

(IV) and ethyl pentane-**αα**$\epsilon\epsilon$-tetracarboxylate (V) was investigated, since, if the condensation proceeded normally, ethyl ϵ-methoxypentane-**αα**$\delta\delta$-tetracarboxylate (VI) and ethyl ζ-methoxyhexane-**αα**$\epsilon\epsilon$-tetracarboxylate (VII) should be formed:

$$(CO_2Et)_2CH\cdot[CH_2]_2\cdot CH(CO_2Et)_2 \longrightarrow \underset{\text{(IV.)}}{}$$

$$OMe\cdot CH_2\cdot C(CO_2Et)_2\cdot[CH_2]_2\cdot CH(CO_2Et)_2. \quad \text{(VI.)}$$

$$(CO_2Et)_2CH\cdot[CH_2]_3\cdot CH(CO_2Et)_2 \longrightarrow \underset{\text{(V.)}}{}$$

$$OMe\cdot CH_2\cdot C(CO_2Et)_2\cdot[CH_2]_3\cdot CH(CO_2Et)_2. \quad \text{(VII.)}$$

When the sodium derivative of ethyl butane-**αα**$\delta\delta$-tetracarboxylate was condensed with monochloromethyl ether, the sole product of the reaction which could be isolated in a pure state was found to be *ethyl* **α**ζ*-dimethoxyhexane-*$\beta\beta\epsilon\epsilon$*-tetracarboxylate*, $C_2H_4[C(CO_2Et)_2\cdot CH_2\cdot OMe]_2$, two molecules of monochloromethyl ether having condensed with one molecule of the disodium derivative of the ester. Only a very small quantity of this ester was isolated in a pure state, when it was obtained in colourless prisms, melting at 92—93°, and yielded on hydrolysis with hydrochloric acid an unsaturated acid, melting at 180—181°, which was in all probability $\Delta^{\alpha\epsilon}$*-hexadiene-*$\beta\epsilon$*-dicarboxylic acid* (VIII).

The main product of the reaction was an oil, which boiled constantly at 225°/13 mm., and on hydrolysis yielded a mixture of adipic acid and a substance melting sharply at 112°. For some time this was thought to be the expected pentene acid, since the analytical data obtained agreed well with that calculated for such an acid. On carefully investigating the properties of this acid, it was, however, clearly shown to be a mixture. On reduction, the only product which could be isolated was adipic acid, whilst on oxidation with potassium permanganate, followed by chromic acid, it yielded a mixture of succinic and adipic acids. This result is only explicable on the assumption that the substance oxidised was a mixture of adipic acid and $\Delta^{\alpha\epsilon}$-hexadiene-$\beta\epsilon$-dicarboxylic acid (VIII):

$$CH_2{:}C(CO_2H)\cdot CH_2\cdot CH_2\cdot C(CO_2H){:}CH_2 \longrightarrow \underset{\text{(VIII.)}}{}$$

$$CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H.$$

It may be pointed out that the analytical data obtained agree well with the supposition that the substance melting at 112° is an equimolecular mixture of adipic acid and the hexadienedicarboxylic acid. It was unfortunate that sufficient of the hexadiene-

dicarboxylic acid was not obtained to test this conclusion experimentally.

When the sodium derivative of ethyl pentane-*aaεε*-tetracarboxylate (V) was condensed with monochloromethyl ether, the reaction proceeded in the expected direction, and *ethyl ζ-methoxyhexane-aaεε-tetracarboxylate* (VII) was formed. This ester could not be separated from unchanged ester, but the products after hydrolysis, pimelic acid and *Δ^{α}-hexene-βζ-dicarboxylic acid*, $CH_2{:}C(CO_2H)\cdot[CH_2]_4\cdot CO_2H$, could readily be separated by crystallisation, first from benzene and finally from hydrochloric acid. The constitution of the hexenedicarboxylic acid was proved by the fact that on oxidation it yielded adipic acid.

Unfortunately, owing to the impossibility of obtaining further material, these experiments are not so complete as it had been hoped to make them, but they appear to indicate clearly that the method used by the author (*loc. cit.*) for the preparation of *cis-cyclo*butane-1 : 3-dicarboxylic acid is not of general application.

Experimental.

Condensation of Monochloromethyl Ether and the Sodium Derivative of Ethyl Ethane-αββ-tricarboxylate.

Ethyl γ-Methoxypropane-αββ-tricarboxylate, $OMe\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CO_2Et$.

In carrying out this condensation, the following method was found to give the most satisfactory results. Finely divided sodium (5·6 grams) was suspended in dry benzene, and ethyl ethane-αββ-tricarboxylate (60 grams) was added; when the vigorous reaction which ensued had ceased, monochloromethyl ether (20 grams) dissolved in an equal volume of benzene was added to the well-cooled solution, with constant shaking. The sodium compound gradually passed into solution, and the benzene became gelatinous, owing to the formation of colloidal sodium chloride. After keeping in the cold overnight, water was added, the benzene separated, dried, and evaporated, and the residual oil fractionated under diminished pressure (12 mm.), when practically the whole passed over at 172—175°. (Yield, 55 grams.) For analysis, the oil was redistilled, when *ethyl γ-methoxypropane-αββ-tricarboxylate* was obtained as a mobile oil, boiling at 161°/7 mm.:

0·1223 gave 0·2400 CO_2 and 0·0874 H_2O. C = 53·5; H = 7·9.
$C_{13}H_{22}O_7$ requires C = 53·7; H = 7·6 per cent.

Hydrolysis of Ethyl γ-Methoxypropane-αββ-tricarboxylate.

(1) *With Hydrochloric Acid. Formation of Itaconic Acid.*—In one experiment the ester (2 grams) was mixed with 20 c.c. of hydrochloric acid (50 per cent.), and heated on the sand-bath in a reflux apparatus for five hours. The ester slowly passed into solution, with the evolution of carbon dioxide, and, on removing the excess of acid on the water-bath, a solid remained, which crystallised from water in well-defined, rhombic octahedra, melting at 161—162°. This acid was found to be itaconic acid, since, on admixture with a specimen of itaconic acid from another source, the melting point was unaltered. As a further confirmation, the silver salt was analysed. (Found, Ag = 62·5. Calc., Ag = 62·8 per cent.)

(2) *With Potassium Hydroxide. Formation of γ-Methoxypropane-αββ-tricarboxylic Acid,* $OMe{\cdot}CH_2{\cdot}C(CO_2H)_2{\cdot}CH_2{\cdot}CO_2H$. —Ethyl γ-methoxypropane-αββ-tricarboxylate (5 grams) was mixed with alcoholic potassium hydroxide (KOH, 8 grams), and heated on the water-bath for one hour, when a gelatinous potassium salt had separated. The solution was diluted with water, saturated with carbon dioxide, and the alcohol completely removed on the water-bath; the solution was then acidified and thoroughly extracted with ether. The ethereal solution was dried and evaporated, when a viscid oil remained, which, on keeping in a vacuum desiccator, completely solidified. For analysis it was purified by crystallisation from a mixture of ether and benzene:

0·1232 gave 0·1848 CO_2 and 0·0544 H_2O. C = 40·9; H = 4·9.
0·1982 „ 0·1993 AgI. OMe = 13·3.
$C_7H_{10}O_7$ requires C = 40·8; H = 4·8; OMe = 15·0 per cent.

γ-Methoxypropane-αββ-tricarboxylic acid crystallises in chalky crusts, which under the microscope are seen to consist of balls of slender needles. It decomposes at 145—146°, with vigorous evolution of carbon dioxide. It is very readily soluble in water, acetone, or ether, but more sparingly so in benzene or chloroform.

The *silver* salt, prepared in the usual manner, was obtained as a flocculent, white precipitate. It is only sparingly soluble in hot water:

0·3186 gave 0·1946 Ag. Ag = 61·1.
$C_7H_7O_7Ag_3$ requires Ag = 61·5 per cent.

γ-Methoxypropane-αβ-dicarboxylic Acid,
$CO_2H{\cdot}CH(CH_2{\cdot}OMe){\cdot}CH_2{\cdot}CO_2H$.

For the preparation of this acid, γ-methoxypropane-αββ-tricarboxylic acid was heated at 150° until all evolution of carbon

dioxide had ceased, when a viscid oil was obtained, which rapidly solidified. It was purified by repeated crystallisation from a mixture of ether and benzene:

0·1118 gave 0·1833 CO_2 and 0·0601 H_2O. C = 44·7; H = 6·0.
0·2767 „ 0·3820 AgI. OMe = 18·2.
$C_6H_{10}O_5$ requires C = 44·4; H = 6·2; OMe = 19·1 per cent.

γ-Methoxypropane-αβ-dicarboxylic acid crystallises in nodules of slender needles, melting at 102°. It is very readily soluble in water and ether, but only sparingly so in benzene and chloroform.

The *silver* salt separated in microscopic plates, which are very sparingly soluble in hot water:

0·2110 gave 0·1204 Ag. Ag = 57·1.
$C_6H_8O_5Ag_2$ requires Ag = 57·4 per cent.

When γ-methoxypropane-αβ-dicarboxylic acid was heated for some time with hydriodic acid, and the excess of acid removed on the water-bath, γ-iodopropane-αβ-dicarboxylic acid was obtained. This acid melted at 139—140° (Swarts, *Jahresber.*, 1866, 722, gives 135°). (Found, I = 48·6. Calc., I = 49·2 per cent.) The corresponding bromo-acid was formed when the methoxy-acid was heated at 150° with hydrogen bromide in a sealed tube. It was obtained in prisms, melting at 137°. (Found, Br = 37·8. Calc., Br = 37·9 per cent.) (Beer, *Annalen*, 1882, **216**, 79, gives the melting point as 137°.)

Distillation of γ-Methoxypropane-αβ-dicarboxylic Acid. Formation of Citraconic Acid.—This experiment was carried out with the object of preparing the anhydride of the methoxy-acid. γ-Methoxypropane-αβ-dicarboxylic acid distils under ordinary pressure between 210° and 230°, a little water distilling below 150°. On carefully fractionating the resulting oil, a considerable fraction was obtained, which distilled at 215—217°/764 mm., and evidently consisted of citraconic anhydride, which is stated to boil at 213—214° (Anschütz, *Ber.*, 1880, **13**, 1542). This was confirmed by converting the anhydride into the acid, which melted at 90—91°, and this melting point was unaltered by admixture with citraconic acid from another source. The presence of a small quantity of an anhydride having a higher boiling point was observed, but it could not be isolated in a pure state. It is clear that the main product of the action of heat on the methoxy-acid is citraconic anhydride.

Action of Acetyl Chloride on γ-Methoxypropane-αβ-dicarboxylic Acid.—The acid (10 grams) was mixed with acetyl chloride (30 grams), and the mixture heated in a sealed tube for three hours at 150—160°. On removing the excess of acetyl chloride, a deep

brown oil was obtained, which did not solidify even on long keeping; on the addition of a little water, however, it rapidly crystallised. (Yield, 9 grams.) On recrystallisation from a little water it was obtained in large, hexagonal prisms, melting at 140—141°, and evidently consisted of γ-chloropropane-αβ-dicarboxylic acid (compare Swarts, *Jahresber.*, 1866, 721). (Found, Cl = 20·9. Calc., Cl = 21·3 per cent.) This acid was found to be the sole product of the action of acetyl chloride on the methoxy-acid, and, as has already been pointed out (see p. 784), its formation is somewhat remarkable.

Action of Potassium Hydroxide on γ-Bromopropane-αβ-dicarboxylic Acid. Formation of Mesaconic Acid.—The reasons which led to the investigation of this reaction have already been given (p. 784). In one experiment the bromo-acid (12 grams) was mixed with alcoholic potassium hydroxide (KOH, 24 grams), and the mixture heated in a reflux apparatus on the water-bath for eight hours, when a considerable quantity of potassium bromide had separated. After removing the alcohol, the aqueous solution was acidified and extracted with ether, and the ether was dried and evaporated, when the acid was obtained as a crystalline cake. This was purified by crystallisation from ether, when it separated in starry needles, melting at 199°, and evidently consisted of mesaconic acid, since this melting point was not depressed when the acid was mixed with mesaconic acid derived from another source. The mother liquors from which the mesaconic acid had separated were very carefully examined to see if any other acid was present, but apparently this unsaturated acid was the sole product of the reaction, no trace of any other acid being observed.

Condensation of Ethyl Butane-ααδδ-tetracarboxylate and Monochloromethyl Ether.

In one experiment, finely divided sodium (2·3 grams) was suspended in benzene (300 c.c.), and ethyl butane-ααδδ-tetracarboxylate (34·6 grams) was added. The sodium gradually passed into solution, and, after keeping overnight, the formation of the sodium derivative was apparently complete. Monochloromethyl ether (10 grams) dissolved in an equal volume of benzene was then slowly added, with constant shaking, to the well-cooled mixture. The reaction took place slowly, but in about half an hour the solution began to become viscous, owing to the separation of sodium chloride. After keeping overnight, the reaction was completed by heating for half an hour on the water-bath. Water was then added, the benzene separated, dried, and evaporated, and the residual oil distilled under diminished pressure (20 mm.), when the

main fraction was found to pass over at 220—240°. After repeated distillation, a fraction was obtained which boiled constantly at 225°/13 mm. This was, however, not a pure substance, and was found to be an inseparable mixture of ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate and ethyl $\alpha\zeta$-dimethoxyhexane-$\beta\beta\epsilon\epsilon$-tetracarboxylate (see below).

A small quantity of an oil, boiling at a somewhat higher temperature, 230—240°/13 mm., slowly deposited crystals on keeping. These were collected, and, after crystallisation from dilute alcohol, the substance was obtained in prisms, melting at 92—93°. For analysis it was dried in a vacuum over sulphuric acid:

0·1134 gave 0·2288 CO_2 and 0·0768 H_2O. C = 55·0; H = 7·5.

$C_{20}H_{34}O_{10}$ requires C = 55·3; H = 7·8 per cent.

This ester was evidently *ethyl* $\alpha\zeta$*-dimethoxyhexane-*$\beta\beta\epsilon\epsilon$*-tetracarboxylate*, having been formed by the condensation of two molecules of monochloromethyl ether with one molecule of the disodium derivative of ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate.

When hydrolysed by boiling for three days on the sand-bath with concentrated hydrochloric acid, the ester passed into solution, and, on cooling, an acid crystallised. This was collected and purified by crystallisation from hot water, in which it was not very readily soluble:

0·1159 gave 0·2380 CO_2 and 0·0592 H_2O. C = 56·0; H = 5·7.

$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

$\Delta^{\alpha\epsilon}$*-Hexadiene-*$\beta\epsilon$*-dicarboxylic acid* separates from water in woolly needles, melting at 180—181°.

The *silver* salt, prepared in the usual manner, separated as a caseous, white precipitate:

0·1512 gave 0·0845 Ag. Ag = 55·9.

$C_8H_8O_4Ag_2$ requires Ag = 56·3 per cent.

The main product of the condensation, which boiled at 225°/13 mm., was hydrolysed by boiling with hydrochloric acid, and, on removal of the excess of acid, an oil remained, which almost completely solidified. After draining on porous porcelain, it was crystallised from a large volume of hot benzene, in which a portion was found to be very sparingly soluble, and consisted of adipic acid. On cooling, the benzene solution deposited a substance which crystallised in fine needles, melting sharply at 112°, and this melting point was not altered by repeated crystallisation. A careful examination of this substance showed, however, that it was a mixture, in spite of the fact that the analytical data obtained (Found, C = 52·8; H = 6·5; Ag = 58·3. $C_7H_{10}O_4$ requires C = 53·2; H = 6·3; Ag = 58·1 per cent.) seemed to point to it being the

expected pentenedicarboxylic acid. When it was reduced with hydrogen in the presence of colloidal palladium, or by means of sodium amalgam, only adipic acid could be isolated. Further, when oxidised with potassium permanganate, followed by chromic acid, it yielded a mixture of adipic and succinic acids. There can, therefore, be little doubt that this substance was simply a eutectic mixture of adipic acid and the hexadienedicarboxylic acid described above. Unfortunately, owing to the small amount of material available, it was not possible to attempt a separation of the two acids.

Condensation of Ethyl Pentane-αaεε-tetracarboxylate and Monochloromethyl Ether.

The sodium derivative of ethyl pentane-αaεε-tetracarboxylate was condensed with monochloromethyl ether in a manner identical with that used in the case of the butane ester. An oil was thus obtained, which boiled constantly at 220—222°/5 mm. Analysis indicated that this ester was a mixture of unchanged ethyl pentane-αaεε-tetracarboxylate and *ethyl ζ-methoxyhexane-αaεε-tetracarboxylate*, and this conclusion was confirmed on hydrolysis with hydrochloric acid.

In one experiment the ester (5 grams) was mixed with hydrochloric acid (50 c.c.) and water (25 c.c.), and heated in a reflux apparatus on the sand-bath until the hydrolysis was complete. On removing the excess of acid, an oil was obtained, which rapidly solidified. After draining on porous porcelain, the acid was crystallised from benzene, when a solid separated in needles, melting at 95—98°; after recrystallisation from a little hot water, the melting point was found to be 104—105°. This substance evidently consisted of pimelic acid, and the identity was confirmed by the method of mixed melting points. The benzene solution from which the pimelic acid had separated was evaporated to dryness, and the residue repeatedly crystallised from hydrochloric acid, and finally from a mixture of ether and light petroleum, from which the pure acid separated in small plates, melting at 77—79°:

0·1158 gave 0·2366 CO_2 and 0·0722 H_2O. C = 55·7; H = 6·9.
$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

$\Delta^{\alpha\varepsilon}$-*Hexene-βζ-dicarboxylic acid* is very readily soluble in ether, benzene, and chloroform, somewhat readily so in water, but only sparingly in light petroleum. In chloroform solution it readily absorbs bromine, and its alkaline solution immediately decolorises a solution of potassium permanganate.

On titration, 0·1029 gram neutralised 0·1018 gram of $Ba(OH)_2$, whereas this quantity of a dibasic acid, $C_8H_{12}O_4$, should neutralise 0·1025 gram.

Oxidation of Δ^{α}*-Hexene-*$\beta\zeta$*-dicarboxylic Acid.*—The acid (5 grams) was dissolved in dilute sodium carbonate solution, and, after the addition of powdered ice, potassium permanganate solution was added until an excess was present. This was removed with a little sulphur dioxide, the manganese dioxide filtered off, the filtrate concentrated, acidified, and repeatedly extracted with ether. On removal of the ether an oil was obtained, which was oxidised with a small quantity of chromic acid solution. The oxidation product was isolated by extraction with ether, and the ether removed, when a solid remained which, after crystallisation from water, melted at 147—149°; the melting point was not altered by admixture with an equal quantity of adipic acid obtained from another source. Since adipic acid was the sole product of the oxidation, there can be no doubt that the hexenedicarboxylic acid has the double linking in the $\alpha\beta$-position.

PRESIDENCY COLLEGE,
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[*Received, April 26th,* 1915.]

LXXXIII.—*Condensation of Ethyl Cyanoacetate and Acetylacetone.*

By JOHN LIONEL SIMONSEN and MUDLAGIRI NAYAK.

ONE of the more important stereochemical problems remaining to be solved is the resolution of an allene derivative of the general formula

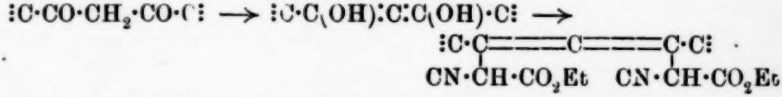
$$\begin{matrix} X \\ Y \end{matrix}\!\!>\!C{:}C{:}C\!<\!\!\begin{matrix} W \\ Z \end{matrix},$$

which, according to van't Hoff, should be capable of exhibiting the phenomena of enantiomorphous isomerism associated with optical activity, although no asymmetric atom is present.

It has been shown by Harding, Haworth and Perkin (T., 1908, **93**, 1944; see also Haworth, T., 1909, **95**, 480) that ethyl cyanoacetate readily condenses with ketones and aldehydes in the presence of secondary amines or sodium ethoxide in accordance with the following scheme:

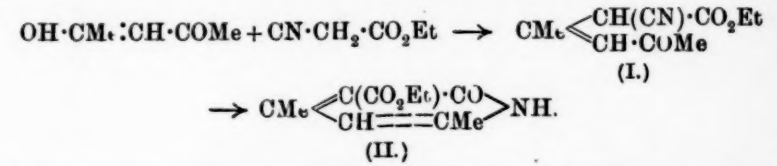
$$>C{:}C(OH)\cdot C{:} + CN\cdot CH_2\cdot CO_2Et \longrightarrow >C{:}\overset{\displaystyle CN\cdot CH\cdot CO_2Et}{\overset{|}{C}}\cdot C{:}$$

It therefore occurred to the authors that it might be possible to condense together ethyl cyanoacetate and a diketone, when, if the reaction followed the same course, an allene derivative should result.

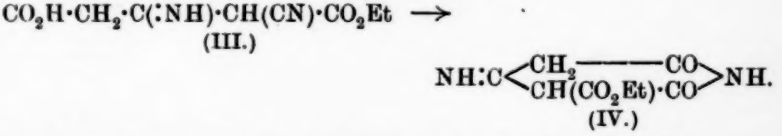


With this object in view, the condensation of ethyl cyanoacetate and acetylacetone has been investigated. Unfortunately, however, the condensation was found to proceed in a quite different manner.

When ethyl cyanoacetate and acetylacetone are condensed together under the conditions described in the experimental part of this paper (p. 794), the main product of the reaction is ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate (II). The mechanism of the formation of this substance would appear to be the following:



One molecule of ethyl cyanoacetate and one of acetylacetone react in the expected manner, with the formation of *ethyl α-cyano-δ-keto-β-methyl-Δ^{α}-hexenoate* (I), which then undergoes molecular rearrangement, with the formation of the pyridone derivative (II). This formation of a pyridone is similar to that investigated by Thorpe and his collaborators (Baron, Remfry and Thorpe, T., 1904, **85**, 1730), who found that ethyl hydrogen β-imino-α-cyano-glutarate (III), on heating at a few degrees above its melting point, yielded ethyl glutazinecarboxylate (IV):



In the case investigated by Thorpe, it was the carboxyl and cyano-groups that underwent intramolecular change, and this, so far as we are aware, is the first occasion in which such a change has been observed to take place with the interaction of a keto-group.

Ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate has been previously prepared by Knoevenagel and Cremer (*Ber.*, 1902, **35**, 2393) by the condensation of ethyl malonate and aminoacetylacetone. The substance obtained by us showed properties identical with those

described, and the identity was further confirmed by the conversion of the ester into 4: 6-dimethyl-2-pyridone-3-carboxylic acid and ψ-lutidocarbostyril.

When the sodium derivative of ethyl 4: 6-dimethyl-2-pyridone-3-carboxylate was treated with methyl iodide, *ethyl* 1: 4: 6-*trimethyl-2-pyridone-3-carboxylate* was formed, the imino-group undergoing methylation. That this was the case was shown by the fact that on hydrolysis and removal of carbon dioxide, 1: 4: 6-trimethyl-2-pyridone was formed, a substance previously prepared by Hantzsch (*Ber.*, 1884, **17**, 1026).

From the mother liquors from which ethyl 4: 6-dimethyl-2-pyridone-3-carboxylate had been separated, a small quantity of a substance was isolated which was only sparingly soluble in alcohol, and crystallised in needles, melting at 191°. This substance appeared to have the composition $C_{12}H_{14}O_2N_2$, and on treatment with bromine yielded a yellow bromo-derivative having the formula $C_{12}H_{13}O_2N_2Br$. Owing to the very small quantity of this substance that we had at our disposal, we were unable to subject it to a detailed examination, but we suggest that it may be *ethyl* $\alpha\epsilon$-*dicyano*-$\beta\delta$-*dimethyl*-$\Delta^{\beta\delta}_{\gamma}$-*hexadienoate* (V), a substance that might be formed by the interaction of two molecules of ethyl cyanoacetate with one of acetylacetone, with the elimination of a carbethoxy-group:

$$OH\cdot CMe{:}C{:}CMe\cdot OH \longrightarrow C\begin{matrix}\nearrow CMe\cdot CH(CN)\cdot CO_2Et\\ \searrow CMe\cdot CH(CN)\cdot CO_2Et\end{matrix} \longrightarrow$$

$$CH\begin{matrix}\nearrow CMe\cdot CH(CN)\cdot CO_2Et\\ \searrow CMe{:}CH\cdot CN\end{matrix} \longrightarrow CH\begin{matrix}\nearrow CMe\cdot CBr(CN)\cdot CO_2Et\\ \searrow CMe{:}CH\cdot CN\end{matrix}$$

(V.) (VI.)

If this is the case, the bromo-derivative would probably be *ethyl* α-*bromo*-$\alpha\epsilon$-*dicyano*-$\beta\delta$-*dimethyl*-$\Delta^{\beta\delta}$-*hexadienoate* (VI). It is proposed to condense ethyl cyanoacetate with various other diketones with a view to ascertain whether this method may be employed for the preparation of allene derivatives.

Experimental.

Condensation of Ethyl Cyanoacetate and Acetylacetone.

Ethyl cyanoacetate (22 grams) was mixed with acetylacetone (20 grams), and, after the addition of diethylamine (2 grams), the mixture, which became slightly warm, was kept in the cold overnight. The pale, reddish-brown solution was then heated on the water-bath for twelve hours, and the crystals which separated on cooling were collected and, after being washed with ether, were drained on porous porcelain. To the filtrate, a further quantity of diethylamine (2 grams) was added, the solution was again

heated for twelve hours on the water-bath, and the crystals which separated on cooling were collected. This process was repeated until no further solid could be obtained. The yield was 17 grams. The crystals obtained in this manner melted indefinitely at 120—130°, and evidently consisted of a mixture. On crystallising from a mixture of chloroform and benzene, the main product of the reaction was obtained in slender needles, melting at 135—136°, and evidently consisted of ethyl 4: 6-dimethyl-2-pyridone-3-carboxylate. [Found, C = 61·9; H = 6·8. $C_{10}H_{13}O_3N$ requires C = 61·5; H = 6·7 per cent.]

The identity of this substance was confirmed by the fact that on hydrolysis with aqueous potassium hydroxide solution it yielded 4: 6-dimethyl-2-pyridone-3-carboxylic acid, which separated from alcohol in fine, iridescent needles, decomposing at 247° (Knoevenagel and Cremer, *loc. cit.*, give 254°). We found that the acid crystallised with one molecule of water of crystallisation, and this may account for the slightly lower melting point observed by us. [Found, C = 57·4; H = 6·1; H_2O = 10·1. $C_8H_9O_3N$ requires C = 57·5; H = 5·4. $C_8H_9O_3N,H_2O$ requires H_2O = 9·7 per cent.]

When ethyl 4: 6-dimethyl-2-pyridone-3-carboxylate was hydrolysed with hydrochloric acid, and the excess of acid removed on the water-bath, ψ-lutidocarbostyril hydrochloride was obtained. This substance was purified by crystallisation from hydrochloric acid, when it separated in small, glistening prisms, melting at 127°. [Found, C = 48·1; H = 7·2; Cl = 20·1. C_7H_9ON,HCl,H_2O requires C = 47·4; H = 6·8; Cl = 20·0 per cent.]

ψ-Lutidocarbostyril hydrochloride has been previously mentioned by Hantzsch (*Ber.*, 1884, **17**, 2904), who stated that it crystallised with two molecules of water of crystallisation, a statement based merely on a halogen estimation. An attempt to estimate the water of crystallisation directly was unsuccessful, since dissociation took place on drying at 100° or in a vacuum.

The free base, which was isolated by shaking the hydrochloride with silver oxide, melted, as stated in the literature, at 180°. [Found, N = 10·9. Calc., N = 11·4 per cent.]

The *picrate*, which does not seem to have been prepared, separated from water, in which it was only sparingly soluble, in glistening, yellow prisms, melting at 155—156°:

0·1032 gave 14·7 c.c. N_2 at 29·6° and 760 mm. N = 15·4.
$C_7H_9ON,C_6H_3O_7N_3$ requires N = 15·9 per cent.

Ethyl 5-*bromo*-4: 6-*dimethyl*-2-*pyridone*-3-*carboxylate*.—For the preparation of this substance, the ester (0·5 gram) was dissolved in chloroform (5 c.c.) and treated with an excess of a chloroform

solution of bromine. Very little heat was generated, and in a short time the liquid became pasty, owing to the separation of a yellow bromo-compound. This was collected, and appeared to be a perbromide, since on exposure to the air bromine was evolved and a colourless substance remained. All attempts to isolate this perbromide in a pure state were unsuccessful, owing to the ease with which bromine was eliminated. The colourless bromide was purified by crystallisation from ethyl acetate:

0·1035 gave 0·1656 CO_2 and 0·045 H_2O. C = 43·6; H = 4·8.
0·1291 „ 0·09 AgBr. Br = 29·8.
$C_{10}H_{12}O_3NBr$ requires C = 44·1; H = 4·4; Br = 29·4 per cent.

Ethyl 5-*bromo*-4: 6-*dimethyl*-2-*pyridone*-3-*carboxylate* separates from ethyl acetate in silky needles, melting at 199°. It is insoluble in water, sparingly so in cold ethyl acetate or benzene, and readily in acetone, chloroform, formic acid, or hot ethyl acetate. It is soluble in potassium carbonate and potassium hydroxide solutions, and may be precipitated unchanged on acidification. On warming with alkalis, however, it is hydrolysed, with the formation of 5-*bromo*-4: 6-*dimethyl*-2-*pyridone*-3-*carboxylic acid*.

This acid was also readily obtained by treating 4: 6-dimethyl-2-pyridone-3-carboxylic acid dissolved in acetic acid with the calculated quantity of bromine dissolved in acetic acid, when the *bromo*-acid separated as a sparingly soluble, crystalline powder. This was collected and crystallised from alcohol, when it was obtained in glistening leaflets, decomposing at 255—256°:

0·1206 gave 0·1740 CO_2 and 0·0380 H_2O. C = 30·4; H = 3·5.
$C_8H_8O_3NBr$ requires C = 39·0; H = 3·2 per cent.

Methylation of Ethyl 4: 6-*Dimethyl*-2-*pyridone*-3-*carboxylate*. 1: 4: 6-*Trimethyl*-2-*pyridone*-3-*carboxylic Acid*.

To a solution of sodium (0·23 gram) in methyl alcohol (10 c.c.) ethyl 4: 6-dimethyl-2-pyridone-3-carboxylate was added, when the sodium compound separated as a crystalline solid. On the addition of methyl iodide (1·5 grams), the sodium compound gradually dissolved, and, after keeping overnight, the clear solution was evaporated to dryness on the water-bath. The crystalline residue was extracted with chloroform, and the chloroform filtered from the sodium iodide, dried, and evaporated. The methylated product was not purified, since it appeared to be a mixture of the ethyl and methyl esters of the acid. The crude ester (1 gram) was mixed with aqueous potassium hydroxide solution (KOH, 2 grams) and heated for half an hour on the sand-bath. On

acidification, the acid separated as a voluminous mass of needles, which were collected and purified by crystallisation from alcohol:

0·1157 gave 0·2554 CO_2 and 0·0660 H_2O. C = 60·2; H = 6·3.
$C_9H_{11}O_3N$ requires C = 59·7; H = 6·1 per cent.

1 : 4 : 6-*Trimethyl-2-pyridone-3-carboxylic acid* separates from alcohol in slender, iridescent needles, melting at 210°. The acid is sparingly soluble in water, alcohol, benzene, ethyl acetate, or acetone, but dissolves more readily in acetic acid or hot alcohol. With ferric chloride solution it gives no colour in the cold, but on warming a faint red coloration is developed. When warmed with hydriodic acid in the Zeisel apparatus, no methyl iodide is evolved. The *copper* and *lead* salts were found to be sparingly soluble, the former crystallising in slender, pale blue needles, the latter in colourless prisms.

On titration, it was found that 0·0911 gram neutralised 0·0791 gram of $Ba(OH)_2,8H_2O$, whereas a monobasic acid, $C_9H_{11}O_3N$, should neutralise 0·0793 gram.

That this acid has the constitution ascribed to it was further shown by the fact that, when heated at about 270°, it lost carbon dioxide and yielded 1 : 4 : 6-trimethyl-2-pyridone. Owing to the hygroscopic character of the pyridone, it was not purified, but was converted into 3 : 5-dibromo-1 : 4 : 6-trimethyl-2-pyridone, which separated from dilute alcohol in needles, melting at 169—170°, whereas Hantzsch (*loc. cit.*) states that this substance melts at 173°. [Found, Br = 54·4. Calc., Br = 54·2 per cent.]

Ethyl αε-*Dicyano-*βδ-*dimethyl-*$\Delta^{\beta\delta}$-*hexadienoate* (V).

The main product of the condensation of ethyl cyanoacetate and acetylacetone was ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate, but a careful examination of the mother-liquors from which this had separated revealed a small quantity of a second substance which, for the reasons given above (p. 794), we consider may possibly be *ethyl* αε-*dicyano-*βδ-*dimethyl-*$\Delta^{\beta\delta}$-*hexadienoate*. This was purified by repeated crystallisation from alcohol, in which it was somewhat sparingly soluble in the cold. For analysis it was dried at 100°:

0·1050 gave 0·2565 CO_2 and 0·0616 H_2O. C = 66·6; H = 6·5.
0·1127 „ 0·2742 CO_2 „ 0·0690 H_2O. C = 66·3; H = 6·8.
0·1163 „ 12·9 c.c. N_2 at 29·5° and 760 mm. N = 12·1.
$C_{12}H_{14}O_2N_2$ requires C = 66·1; H = 6·4; N = 12·8 per cent.

The ester separates from alcohol in slender needles, melting at 190—191°. When it was hydrolysed with potassium hydroxide solution or barium hydroxide solution, ammonia is evolved, and

the ester appears to undergo complete disintegration, since on acidification and extraction only a small trace of an oil could be isolated.

In chloroform solution, bromine is readily absorbed, and on evaporation of the solvent an oily bromo-derivative was obtained. This was dissolved in hot ethyl acetate, and, on cooling, a substance separated in fine yellow needles, melting at 196°:

0·1176 gave 0·2093 CO_2 and 0·0448 H_2O. C = 48·5; H = 4·2.

0·1438 „ 0·0898 AgBr. Br = 26·6.

$C_{12}H_{13}O_2N_2Br$ requires C = 48·5; H = 4·4; Br = 26·9 per cent.

This substance was possibly *ethyl α-bromo-αε-dicyano-ββδ-dimethyl-*$\Delta^{\beta\delta}$*-hexadienoate*. The mother liquor from which this bromo-ester was obtained contained more highly brominated substances, which were, however, present in too small a quantity to be isolated in a pure state.

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[*Received, April 26th*, 1915.]

LXXXIV.—*Resolution of Externally Compensated* p-*Toluenesulphonylalanine into its Optically Active Components.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

VARIOUS modifications of the equilibrium method have been applied to the resolution of externally compensated bases, chiefly by Pope and his co-workers (T., 1899, **75**, 1066, 1093; 1910, **97**, 2199), but the equilibrium method for the resolution of externally compensated acids has not been worked out so thoroughly.

Some time ago, Pope and Gibson showed that externally compensated benzoylalanine was easily resolved by means of strychnine and brucine (T., 1912, **101**, 939). The method consisted essentially in combining one molecule of strychnine and one molecule of alkali with two molecules of the externally compensated compound, when an almost quantitative yield of the strychnine salt of *d*-benzoylalanine was obtained. The mother liquor, containing an excess of *l*-benzoylalanine, was then acidified, and the precipitated acid treated with the calculated quantity of brucine and alkali. In this way, the brucine salt of *l*-benzoylalanine was easily obtained. The salts were readily purified by crystallisation, and the optically pure *d*- and *l*-benzoylalanines isolated, and obtained

pure in the usual manner. When, however, the alkaloids were employed in the reverse order, it was found that the brucine salt consisted of mixed crystals of the brucine salt of *d*- and *l*-benzoylalanines, which could not be separated by crystallisation. The acid obtained from these crystals consisted of 97·6 per cent. of *l*-benzoylalanine, and this also could not be purified by fractional crystallisation. A similar case has been recorded by Perkin, Pope and Wallach (T., 1909, **95**, 1789) in the resolution of *dl*-1-methyl-*cyclo*hexylidene-4-acetic acid. As the preparation of sulphonyl and carbonyl derivatives of alanine is easily accomplished, it was decided to investigate further the above method of resolution with the objects of determining whether the formation of mixed crystals such as is described above is common, of increasing our knowledge of the methods of resolving externally compensated compounds, and also of gaining some idea of the influence of the exchange of $\cdot SO_2$ for $\cdot CO$ on the optical rotatory power.

In the present case, externally compensated *p*-toluenesulphonylalanine has been resolved in two ways, namely, by using first strychnine and then brucine, and by using these alkaloids in the reverse order. It is found that the compound is completely resolved in either of the above ways, that is, the resolution is entirely reversible, and therefore there was no sign of the formation of mixed crystals.

Experimental.

dl-p-*Toluenesulphonylalanine*, $CH_3 \cdot CH(CO_2H) \cdot NH \cdot SO_2 \cdot C_6H_4 \cdot CH_3$.

This compound has already been described (Pope and Gibson, T., 1912, **101**, 945). It is best prepared in small quantities. Five grams of alanine are treated gradually with 13·7 grams of *p*-toluenesulphonyl chloride and 6·3 grams of potassium hydroxide in normal solution. The mixture is heated, after thoroughly shaking, on the water-bath. The reaction is energetic, and, with careful working, 5 grams of the pure product are obtained, which is recrystallised twice from aqueous alcohol.

First Resolution of dl-p-*Toluenesulphonylalanine.*

Using the equilibrium method, two equivalents of *dl-p*-toluenesulphonylalanine (25 grams), one equivalent of sodium hydroxide (2·06 grams) in normal solution, and one equivalent of brucine (24 grams) were dissolved in just sufficient boiling water, and, after keeping the mixture for some hours, an almost theoretical quantity of the *brucine* salt of *l-p*-toluenesulphonylalanine separated. The mother liquor from the separation of the brucine

salt was evaporated, made alkaline, and the solution extracted thoroughly with chloroform until free from brucine. The solution was then acidified with concentrated hydrochloric acid, and the precipitated crude *d*-acid, which was first obtained as an oil, quickly crystallised. This acid, in the form of the sodium salt in aqueous solution, had the specific rotatory power $[\alpha]_{5461}$ +20·0°, and therefore contained 80 per cent. of the pure *d*-acid. The crude acid (13·1 grams) was accordingly mixed with 13·7 grams of strychnine and 0·5102 gram of sodium hydroxide in normal aqueous solution, and the whole brought into solution with sufficient boiling water. On cooling and keeping for some hours, an almost theoretical quantity of the *strychnine* salt of *d*-*p*-toluenesulphonylalanine was obtained. The resolution was repeated, with practically identical results.

Brucine l-p-*Toluenesulphonylalanine*,
$C_{23}H_{26}O_4N_2,C_{10}H_{13}O_4NS,3H_2O$.

The salt, separated as described, is very easily obtained pure on crystallisation from dilute aqueous alcohol. It was recrystallised four times, although it was found to be pure after two crystallisations. The salt crystallises in large, colourless, glistening plates, which are very brittle. It melts at 148—149°, losing water of crystallisation. It is very sparingly soluble in water, but more readily so in alcohol:

0·1244 gave 0·2601 CO_2 and 0·0729 H_2O. C = 57·0; H = 6·5.
1·020 lost 0·0738 at 130°. H_2O = 7·2.
$C_{10}H_{13}O_4NS,C_{23}H_{26}O_4N_2,3H_2O$ requires C = 57·3; H = 6·5; $3H_2O$ = 7·8 per cent.
0·1928 made up to 30·0 c.c. with absolute alcohol and examined in a 4-dcm. tube at 29—30° gave α_{5461} −0·99°, whence $[\alpha]_{5461}$ −38·51°; $[M]_{5461}$ −266·2°.

Strychnine d-p-*Toluenesulphonylalanine*,
$C_{21}H_{22}O_2N_2,C_{10}H_{13}O_4NS,2H_2O$.

The strychnine salt is far more readily soluble in water than the above brucine salt, and is easily purified by recrystallisation from that solvent. The salt was recrystallised four times. On being allowed to crystallise slowly, it forms large, colourless, glistening prisms, melting at 188—189°; only one molecule of water is lost on heating at 125°:

0·1272 gave 0·2835 CO_2 and 0·0778 H_2O. C = 60·8; H = 6·8.
0·6954 lost 0·0245 at 125°. H_2O = 3·5.
$C_{10}H_{13}O_4NS,C_{21}H_{22}O_2N_2,2H_2O$ requires C = 60·7; H = 6·4; $1H_2O$ = 3·2 per cent.

0·2076 made up to 30·0 c.c. with water and examined in a 4-dcm. tube at 29—30° gave α_{5461} −0·31°, whence $[\alpha]_{5461}$ −11·2°; $[M]_{5461}$ −68·7°.

Second Resolution of dl-p-*Toluenesulphonylalanine.*

This was carried out in an exactly similar manner to the first resolution, using first strychnine and then brucine. The resolution proceeds quite normally, and almost theoretical quantities of the strychnine *d-p*-toluenesulphonylalanine and brucine *l-p*-toluenesulphonylalanine are obtained in this order. The salts were purified as above, and had identical melting points and rotatory powers with those previously described; it was thus easily seen that they were identical. (Found, strychnine salt, m. p. = 188—189°, C = 60·8; H = 6·2; $[\alpha]_{5461}^{29-30}$ −11·3° in water. Brucine salt, m. p. = 148—149°, $[\alpha]_{5461}^{29-30}$ −38·76° in absolute alcohol.)

This method of resolution was repeated, and exactly similar results were obtained. It may be stated that, of the two methods of resolution employed, the second method is to be preferred. In the first method, after the precipitation of the brucine remaining in the solution after the separation of the brucine salt of *l-p*-toluenesulphonylalanine with alkali, unless the filtered liquid is thoroughly extracted with chloroform, the brucine remaining is likely to contaminate the strychnine salt obtained in the next process. This tedious extraction is avoided by first isolating the strychnine salt of *l-p*-toluenesulphonylalanine.

l-p-*Toluenesulphonylalanine*, $CH_3 \cdot CH(CO_2H) \cdot NH \cdot SO_2 \cdot C_6H_4 \cdot CH_3$.

This acid was liberated from the brucine salts obtained in the first and the second resolutions by boiling the salt with an excess of aqueous ammonia, filtering from the precipitated brucine, and extracting the filtrate at least six times with chloroform. The aqueous solution was evaporated to a small bulk on the water-bath, and acidified with concentrated hydrochloric acid. The precipitated acid was at first oily, but quickly solidified on stirring. It was recrystallised three times from very dilute aqueous alcohol. On allowing the solution to evaporate slowly, the acid was obtained in very long, colourless needles, melting at 131—132°. The substance is easily soluble in ethyl alcohol, methyl alcohol, or acetone, but much less readily so in water. It may be crystallised from boiling water:

0·1249 gave 0·2234 CO_2 and 0·0596 H_2O. C = 48·8; H = 5·3.
$C_{10}H_{13}O_4NS$ requires C = 49·3; H = 5·4 per cent.

As was anticipated, the acid from the brucine salt obtained by

the first method of resolution (*a*) was identical with that from the brucine salt obtained in the second resolution (*b*):

(*a*) 0·2018 as sodium salt made up to 30·0 c.c. with water and examined in a 4-dcm. tube at 29—30° gave α_{5461} −0·91°, whence $[\alpha]_{5461}$ −33·8°; $[M]_{5461}$ −82·1°.

(*b*) 0·2020 as sodium salt made up to 30·0 c.c. in water and examined as above gave α_{5461} −0·91°, whence $[\alpha]_{5461}$ −33·8°; $[M]_{5461}$ −82·1°.

The following determinations of rotatory powers were made on the acid obtained from both resolutions:

In water.—0·5116 as sodium salt made up to 30·0 c.c. and examined in a 4-dcm. tube at 29—30° gave α_{5461} −2·41°, $[\alpha]_{5461}$ −35·33°; $[M]_{5461}$ −85·8°.

2·0044 as sodium salt, examined as above, gave α_{5461} −10·7°, $[\alpha]_{5461}$ −40·04°; $[M]_{5461}$ −97·3°.

It will be seen that, as was found in the case of optically active benzoylalanine, the rotatory power of the acid in the form of its salt increases with the concentration; in the present example this increase is very marked.

In absolute ethyl alcohol.—0·0063 made up to 30·0 c.c. and examined in a 4-dcm. tube at 29—30° gave α_{5461} −1·23°, $[\alpha]_{5461}$ −9·17°; $[M]_{5461}$ −22·2°.

In acetone.—1·0006 made up and examined as above gave α_{5461} −1·16°, $[\alpha]_{5461}$ −8·69°; $[M]_{5461}$ −21·1°.

In the case of optically active benzoylalanine, it was observed that the rotatory power in acetone was considerably greater than in alcohol. The above figures show that in the case of *p*-toluenesulphonylalanine the rotatory power in alcohol is almost the same as that in acetone.

d-p-*Toluenesulphonylalanine*, $CH_3 \cdot CH(CO_2H) \cdot NH \cdot SO_2 \cdot C_6H_4 \cdot CH_3$.

This acid was obtained from the strychnine salts obtained in both resolutions by boiling with concentrated aqueous ammonia, allowing to cool, and filtering from the precipitated strychnine. The filtrate was evaporated to a small bulk on the water-bath, and the acid precipitated by the addition of concentrated hydrochloric acid. The acid was then crystallised three times from dilute aqueous alcohol. It was obtained in colourless needles, melting at 131—132°, which often measured as much as 4 cm.:

0·1306 gave 0·2357 CO_2 and 0·0654 H_2O. C=49·2; H=5·6.

$C_{10}H_{13}O_4NS$ requires C=49·4; H=5·4 per cent.

The acid from the strychnine salts obtained in the first resolution (*a*) was proved to be identical with that obtained in the second

resolution (*b*) by a comparison of the melting points and of the rotatory powers.

In water.—(*a*) 0·2009 as sodium salt made up to 30·0 c.c. with water and examined in a 4-dcm. tube at 29—30° gave α_{5461} +0·90°, $[\alpha]_{5461}$ +33·6°; $[M]_{5461}$ +81·6°.

(*b*) 0·2021 as sodium salt made up and examined as above gave α_{5461} +0·91°, $[\alpha]_{5461}$ +33·7°; $[M]_{5461}$ +81·8°.

The solubility of the *d*-acid was exactly similar to that of the *l*-acid, and the acids behave similarly in all respects.

It will be seen that the resolution of externally compensated *p*-toluenesulphonylalanine can be very readily accomplished in either of the above ways, and is not attended with the formation of mixed crystals. Owing to the conditions of working, it has, so far, been impossible to determine the rotatory dispersions. Further work on the resolution of analogous compounds is in progress.

The authors wish to express their thanks to Mr. K. R. Krishna Aiyar for assistance with the determination of optical rotatory powers, and to the Research Fund Committee of the Chemical Society for a grant which has largely covered the expenses of this investigation.

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[*Received, April 26th*, 1915].

LXXXV.—*Condensation of Acid Chlorides with the Ethyl Ester of* (a) *Cyanoacetic Acid*, (b) *Malonic Acid, and* (c) *Acetoacetic Acid. Part. II. Some Experiments on Ethyl Phthaliminoacetoacetate and Ethyl γ-Ethoxyacetoacetate.*

By John Bradshaw, Henry Stephen (1851 Exhibition Scholar), and Charles Weizmann.

In the first part of this research (T., 1913, **103**, 1855) it was shown that the condensation of phthaliminoacetyl chloride with ethyl sodiomalonate gave different products, according to the method of procedure. It was found there that if the condensation took place under the conditions stated by Gabriel (*Ber.*, 1913, **46**, 1319), ethyl phthaliminoacetylmalonate was formed, but if the method described by the authors was employed, the keto-modi-

fication of ethyl phthaliminoacetoacetate was produced, and from this substance the corresponding enol-modification was obtained.

Gabriel and Colman (*Ber.*, 1909, **42**, 1244), and later Pfaehler (*Ber.*, 1913, **46**, 1702), found that on boiling ethyl phthaliminoacetylmalonate with water, ethyl phthaliminoacetoacetate was produced, which melted at 110°. The ketonic modification of this substance, obtained as stated above, melted at 119°, and gave no coloration with ferric chloride; these properties do not agree with those recorded of the substance, m. p. 110°. The latter develops a deep red coloration with ferric chloride, whilst the enolic form of the ester, which melts at 70°, produces an intense violet. It has since been established that the three substances react with phenylhydrazine under similar conditions to produce the same pyrazolone,

$$C_6H_4\begin{<}CO\\CO\end{>}N\cdot CH_2\cdot C\begin{<}CH_2\cdot CO\\N{=}\!-\!-N\end{>}Ph.$$

The condensation of phthaliminoacetyl chloride with ethyl sodiomalonate according to the method described in the former communication can lead to the formation of ethyl bisphthaliminoacetylmalonate, as well as of ethyl phthaliminoacetylmalonate. The separation of these two substances was effected, since the former was less readily soluble in ethyl alcohol than the latter.

The action of phenylhydrazine on each of these substances leads to some interesting results. In the case of the bis-derivative, the action of phenylhydrazine was the same as that described by Scheiber and Reckleben (*Ber.*, 1913, **46**, 2412) for ethyl bissucciniminoacetylmalonate; in the present instance, a mixture of the pyrazolone of ethyl phthaliminoacetylmalonate and the phenylhydrazide of phthaliminoacetic acid was obtained, these substances being separated by treatment with sodium hydroxide solution, in which the former alone is soluble. The same hydrazide was also obtained by the action of phenylhydrazine on phthaliminoacetyl chloride.

Ethyl phthaliminoacetylmalonate, on treatment with phenylhydrazine, yields the pyrazolone mentioned above. The action of hydrolysing agents on the various condensation products has been further investigated, with the following results. When the pure keto-form is distilled in a current of steam during half an hour, the residual oil, which solidifies on cooling, gives a distinct deep red coloration with ferric chloride, but after recrystallisation from ethyl alcohol the product was found to melt at the same temperature as the original substance; the mother liquor, however, still showed the ferric chloride reaction. It is evident that enolisation had taken place. Under similar conditions, the enolic form partly dissolved and partly remained as an oil, which solidified on cool-

ing, and, after twice recrystallising from ethyl alcohol, melted at 110°, and was identical with the substance obtained by Gabriel and Colman (*loc. cit.*). From the aqueous solution, on cooling, crystals of phthaliminoacetic acid were deposited, which, after being recrystallised from hot water, melted at 192°. By treatment of these substances with steam for several hours, phthaliminoacetone was obtained in the first instance, and phthaliminoacetic acid in the other case, together with a small amount of phthaliminoacetone, which was separated from the acid by means of sodium carbonate. A result similar to that first mentioned was obtained by the action of steam for a long period on ethyl phthaliminoacetylmalonate, phthaliminoacetone being obtained.

The treatment of the bis-derivative by the same method gave a mixture of phthaliminoacetic acid and phthaliminoacetone, the former being produced, probably, by the elimination of a phthaliminoacetyl group during the hydrolysis.

Further decomposition of the above substances was obtained by treatment in the following way. The ester under consideration was heated for two hours in a sealed tube at 250°, and the results were as follows. Ethyl phthaliminoacetylmalonate gave a mixture of phthaliminoacetic acid and phthaliminoacetone, ethyl phthaliminoacetoacetate (ketonic form) gave a similar mixture, whilst ethyl phthaliminoacetoacetate (enolic form) yielded phthaliminoacetic acid as the chief product. The bis-derivative behaved as stated above. The action of mineral acids, such as hydrochloric, hydrobromic, or hydriodic acid, is to cause a more complete decomposition of these substances, resulting in the decomposition of the phthalimino-group, as has been shown by Gabriel. In a similar way, the action of alkalis is to attack the phthalimino-group, with the formation of phthalamic acids.

The action of sodium nitrite on ethyl phthaliminoacetylmalonate and on the two acetoacetic ester derivatives gives the same product, namely, α-oximino-γ-phthaliminoacetone. Attempts to prepare α-amino-γ-phthaliminoacetone by reduction of the previous substance with tin or stannous chloride and hydrochloric acid were without result, the hydrochloride of the amino-ketone being unstable, and no salts could be obtained.

In the first part of these investigations a method has been given by which ethyl γ-ethoxyacetoacetate can be obtained, and several derivatives of this substance are now described. α-Oximino-γ-ethoxyacetone, which has been obtained previously, was investigated with a view to its reduction by stannous chloride in acid solution to the corresponding amino-compound. Several attempts were made to obtain this substance, but without results of a

definite value. The course of the reduction seems to be normal, and it is in the isolation of the hydrochloride of the base from the acid solution where the process fails, owing to the fact that the ethoxy-group in the molecule is attacked by the acid during the concentration of the solution, even when the evaporation takes place under diminished pressure. The preparation of such derivatives as the platinum or gold salts or the picrate was impossible from the very impure product obtained, as stated above. It was evident, however, that the amino-ketone had been formed, as the solution reduced Fehling's solution in the cold, and liberated silver from an ammoniacal solution of silver nitrate, and mercury from an alkaline solution of mercuric chloride (compare Gabriel and Pinkus, *Ber.*, 1893, **26**, 2197).

The instability of α-amino-γ-ethoxyacetone is to be considered, therefore, as due to the presence of the ethoxy-group in the molecule. Further instances of this effect will be found in the later experimental work of this paper, but in studying the reactions of α-oximino-γ-ethoxyacetone an interesting case came under observation. On condensation of this substance with *o*-phenylenediamine, the formation of 2-ethoxymethylquinoxaline takes place, and this substance, on oxidation with potassium permanganate, gives pyrazine-2 : 5 : 6-tricarboxylic acid; in no case could 2-ethoxymethylpyrazine-5 : 6-dicarboxylic acid be obtained.

Experimental.

Ethyl Bisphthaliminoacetylmalonate,

$$\left(C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!N\cdot CH_2\cdot CO\right)_2 C(CO_2Et)_2.$$

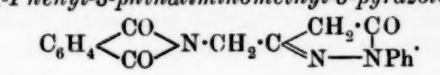
This was obtained in the condensation of phthaliminoacetyl chloride and ethyl sodiomalonate, and was separated from the ethyl phthaliminoacetoacetate by extracting the latter with ethyl alcohol, in which the above substance is only sparingly soluble. The product was then crystallised from ethyl acetate, and was obtained in small, white needles, melting at 176°, which are soluble in acetone and in a mixture of chloroform and light petroleum:

0·1057 gave 0·2372 and 0·0438 H_2O. C = 60·91; H = 4·62.

0·1734 ,, 8·4 c.c. N_2 at 17° and 745 mm. N = 5·5.

$C_{27}H_{22}O_{10}N_2$ requires C = 60·74; H = 4·13; N = 5·2 per cent.

1-Phenyl-3-phthaliminomethyl-5-pyrazolone,



This substance was obtained by the treatment of the enolic or ketonic form of ethyl phthaliminoacetoacetate with phenylhydrazine.

5·5 Grams of the ester were mixed with 2·5 grams of phenylhydrazine. After a short time the mixture became warm, and liquefied. The reaction was completed by warming in the steam-bath for an hour, at the end of which time the product had solidified to a hard cake. This was crystallised from methyl alcohol, and obtained as a fine, crystalline powder, which melted and decomposed at 192°:

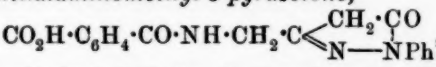
0·1870 gave 0·4571 CO_2 and 0·0768 H_2O. C = 66·66; H = 4·5.

0·1244 „ 15·8 c.c. N_2 at 17° and 758 mm. N = 13·85.

$C_{18}H_{13}O_3N_3$ requires C = 67·2; H = 4·0; N = 13·76 per cent.

Attempts to obtain the corresponding aminomethyl derivative from the above substance have so far been unsuccessful, as only a very impure substance was obtained by boiling it with hydrochloric or hydrobromic acid, or by heating it in a sealed tube at 150° for two hours with the same acids.

1-Phenyl-3-phthalaminomethyl-5-pyrazolone,

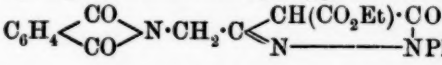


was obtained by hydrolysing the above substance with an alcoholic solution of potassium hydroxide, and treating the resulting potassium salt with hydrochloric acid. It crystallised from dilute acetic acid as a yellow, crystalline powder, melting and decomposing at 164°. The further hydrolysis of this substance with acids did not lead to any better result than that mentioned above:

0·2116 gave 0·4957 CO_2 and 0·0748 H_2O. C = 63·90; H = 3·93.

$C_{18}H_{15}O_4N_3$ requires C = 64·09; H = 4·15 per cent.

Ethyl 1-Phenyl-3-phthaliminomethyl-5-pyrazolone-4-carboxylate,



This compound was obtained by warming phenylhydrazine and ethyl phthaliminoacetylmalonate in 50 per cent. acetic acid solution for a short time on the steam-bath. The product crystallised from acetic acid as a pale yellow powder, which melted at 215°:

0·1041 gave 0·2472 CO_2 and 0·0428 H_2O. C = 64·7; H = 4·5.

0·1285 „ 12·0 c.c. N_2 at 23·5° and 763 mm. N = 10·78.

$C_{21}H_{17}O_5N_3$ requires C = 64·4; H = 4·3; N = 10·7 per cent.

The corresponding phthalamino-derivative was obtained as a yellow, crystalline powder, but not in a condition pure enough for analysis. On fusion at 120°, carbon dioxide was evolved, and from the residue, after crystallisation from acetic acid, the above-described phthalaminopyrazolone, melting at 164°, was obtained. By warming an excess of phenylhydrazine with ethyl bisphthaliminoacetylmalonate in a 50 per cent. solution of acetic acid, a mixture of the pyrazolone just described and the phenylhydrazide of phthaliminoacetic acid was obtained. The crude product was treated with cold sodium hydroxide solution, and the residue, consisting of the hydrazide, was filtered from the alkaline solution and crystallised from ethyl alcohol, being thus obtained in small needles, melting at 197°. This substance was identical with that obtained by the action of phenylhydrazine on phthaliminoacetyl chloride, which crystallised from ethyl alcohol in small needles, melting at 198—199°.

On acidifying the alkaline solution, there was obtained the pyrazolone, melting at 215°, and identical with that already described.

Phthaliminoacetyl Phenylhydrazide,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot CH_2\cdot CO\cdot NH\cdot NHPh.$$

Two grams of phthaliminoacetyl chloride, crystallised from benzene, were treated with 1·5 grams of phenylhydrazine. Reaction took place immediately in the cold, and, after keeping for fifteen minutes, the mixture was warmed on the steam-bath for half an hour. The product crystallised from methyl alcohol in needles, melting at 199°, and gave a violet coloration in the Bülow reaction:

0·1368 gave 0·3260 CO_2 and 0·0519 H_2O. C = 65·00; H = 4·22.
$C_{16}H_{13}O_3N_3$ requires C = 65·08; H = 4·4 per cent.

α-Oximino-γ-phthaliminoacetone,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot CH_2\cdot CO\cdot CH{:}NOH.$$

Ten grams of ethyl phthaliminoacetylmalonate were dissolved in 7 grams of potassium hydroxide contained in 250 c.c. of water, and the clear solution was treated with 2·8 grams of sodium nitrite dissolved in a small quantity of water. The mixed solutions were kept for twenty-four hours, and then treated with a slight excess of dilute sulphuric acid. The crystals which had separated after the solution had been kept for two days in the ice-chamber were recrystallised from benzene and obtained in prisms, melting and decomposing at 156°:

0·1986 gave 0·4092 CO_2 and 0·0776 H_2O. C = 56·62; H = 3·46.
0·2266 ,, 8·8 c.c. N_2 at 19° and 760 mm. N = 4·5.
$C_{11}H_8O_4N_2$ requires C = 57·00; H = 3·40; N = 3·41 per cent.

Ethyl Ethylidenebis-γ-ethoxyacetoacetate, $CHMe[CH(CO_2Et)\cdot CO\cdot CH_2\cdot OEt]_2$.

Thirty-five grams (2 mols.) of ethyl γ-ethoxyacetoacetate were mixed with 4·5 grams (1 mol.) of freshly distilled acetaldehyde, and the whole was well cooled in a freezing mixture of ice and salt. Two grams of diethylamine were then added gradually, the temperature being maintained at 0°. After keeping at this temperature for two hours, the mixture was left at room temperature for five days, when it had formed a crystalline mass. A portion of this, after being pressed on a porous plate, crystallised from methyl alcohol in colourless needles, melting at 96°:

0·2793 gave 0·6012 CO_2 and 0·1812 H_2O. C = 58·71; H = 8·00.
$C_{18}H_{30}O_8$ requires C = 59·34; H = 8·24 per cent.

1-*Ethoxy*-4-*methyl*-2-*ethoxymethyl*cyclo*hexen*-6-*one*,

$$EtO\cdot CH_2\cdot C\begin{matrix}C(OEt)-CO\\ CH_2\cdot CHMe\end{matrix}CH_2.$$

Twenty-seven grams of the crude ester obtained in the preceding condensation were hydrolysed by boiling with dilute sulphuric acid for twenty hours, and the product was distilled in a current of steam. The distillate was treated with solid potassium hydroxide, and the oil thus obtained was extracted with ether, dried, and distilled. Five grams of an oil boiling at 149°/12 mm. were obtained. An attempt to improve the yield was made in the following manner. Twenty-two grams of the ester were dissolved in an equal volume of benzene, and the solution was saturated with hydrogen chloride and kept for twelve hours. The mixture was then poured into water, washed several times with a solution of sodium hydrogen carbonate, and finally with water; it was then dried, and the benzene removed by distillation under diminished pressure. Some hydrogen chloride which was still found to be present was removed by boiling the product with diethylaniline (6 grams) in an oil-bath at 140°. The product was then poured into water and extracted with ether, and the ethereal extract, after being washed several times with dilute sulphuric acid, and finally twice with water, was dried and distilled. The product boiled at 157°/15 mm., and had a pleasant, terpene-like odour. The yield by this method was 8 grams:

0·2463 gave 0·6187 CO_2 and 0·2019 H_2O. C = 67·4; H = 9·11.
$C_{12}H_{20}O_3$ requires C = 67·92; H = 9·43 per cent.

The poor yields in the two methods are probably due to the effect of the acid on the ethoxy-groups, since a considerable amount of substance, which decomposes on distillation at a higher temperature, is produced.

The *semicarbazone* of this *cyclo*hexenone was obtained by dissolving 2·5 grams of sodium acetate in a small quantity of water, and adding 1·5 grams of semicarbazide hydrochloride and 2 grams of the *cyclo*hexenone. The product crystallised from methyl alcohol in plates, melting and decomposing at 232°:

0·1218 gave 16·0 c.c. N_2 at 14° and 760 mm. N = 15·60.
$C_{13}H_{23}O_3N_3$ requires N = 15·61 per cent.

Ethyl γ-Ethoxy-α-methylacetoacetate, $EtO{\cdot}CH_2{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$.

Johnson (*J. Amer. Chem. Soc.*, 1913, **35**, 582) has already described the preparation of this substance, and of the corresponding ethyl compound, by condensing ethyl ethoxyacetate with ethyl α-bromopropionate and ethyl α-bromobutyrate, respectively, in the presence of zinc.

In the present instance, the following method has been adopted.

4·6 Grams (1 atom) of sodium were dissolved in 60 c.c. of ethyl alcohol, and 35 grams (1 mol.) of ethyl γ-ethoxyacetoacetate were gradually added to the solution, cooled in ice, and then 28 grams (1 mol.) of methyl iodide. The mixture was kept for an hour, and afterwards heated on the steam-bath until the solution gave a neutral reaction towards litmus. The product was treated with water, the ester extracted several times with ether, and the ethereal solution dried and distilled after the evaporation of the ether; the bulk of the liquid distilled at 114—120°/14 mm. After carefully fractionating this product, a substance, boiling at 115°/16 mm., was obtained. This, on analysis, proved to be the above compound, which is a pale yellow liquid, but is colourless immediately after distillation. (Found, C = 57·3; H = 8·16. $C_9H_{16}O_4$ requires C = 57·44; H = 8·51 per cent.)

Ethyl γ-ethoxy-α-ethylacetoacetate is obtained in a similar way, using ethyl iodide. It is a pale yellow liquid, boiling at 124°/15 mm.

Ethyl γ-ethoxy-α-propylacetoacetate, $EtO{\cdot}CH_2{\cdot}CO{\cdot}CHPr{\cdot}CO_2Et$, is a colourless liquid, boiling at 137°/18 mm:

0·1554 gave 0·3470 CO_2 and 0·1258 H_2O. C = 60·90; H = 9·02.
$C_{11}H_{20}O_4$ requires C = 61·11; H = 9·26 per cent.

*Ethyl γ-ethoxy-α-iso*propylacetoacetate,
$EtO{\cdot}CH_2{\cdot}CO{\cdot}CHPr^{\beta}{\cdot}CO_2Et$,
boils at 131°/18 mm.:

0·1215 gave 0·2707 CO_2 and 0·0962 H_2O. C = 60·77; H = 8·80.
$C_{11}H_{20}O_4$ requires C = 61·11; H = 9·26 per cent.

Ethyl γ-*ethoxy*-α-iso*butylacetoacetate*,

$$EtO{\cdot}CH_2{\cdot}CO{\cdot}CH(CH_2Pr^{\beta}){\cdot}CO_2Et,$$

boils at 128°/10 mm.:

0·1089 gave 0·2489 CO_2 and 0·0911 H_2O. C = 61·85; H = 9·3.
$C_{12}H_{22}O_4$ requires C = 62·60; H = 9·56 per cent.

The methyl and ethyl derivatives just described were submitted to hydrolysis in various ways in order to obtain the corresponding ketones, but in every case the acid and the undecomposed ester were also present, so that the yield of the ketone was considerably diminished.

Ten grams of the methyl derivative were heated on the steam-bath for two hours with 100 c.c. of a 10 per cent. solution of potassium hydroxide in water. The product was saturated with potassium carbonate, and extracted with ether. After drying, and evaporation of the ether, an oily residue was left, which gave a violet coloration with ferric chloride, showing the presence of unchanged ester. On distillation, a small fraction was obtained boiling at 140—150°, consisting of a colourless liquid having an odour different from that of the original ester. Béhal and Sommelet give the boiling point of α-ethoxybutan-β-one as 146° (*Compt. rend.*, 1904, **138**, 89).

Forty-five grams of the same derivative were divided into three equal portions, and heated in sealed tubes, with twice the volume of water in each case, for one hour at 210°. On opening the tubes, a considerable pressure was observed, and an oily layer, consisting of unchanged ester, was also noted. The contents of the tubes were saturated with potassium carbonate (the first addition produced an effervescence, due to the presence of free acid) and extracted with ether, and, after drying, the ether was evaporated. On distillation, an oil, boiling at 146°, was obtained, which formed a semicarbazone, melting at 87° by Béhal and Sommelet's method (*loc. cit.*).

The corresponding α-ethoxypentan-β-one was obtained from ethyl γ-ethoxy-α-ethylacetoacetate by the method just described, and is an oil boiling at 167° (Béhal and Sommelet give 164—165°). The other alkyl derivatives were hydrolysed in the same way, with the result that "acid" hydrolysis chiefly occurs; this was shown by titrating the acid formed with *N*-sodium hydroxide.

One gram of the propyl and the *iso*propyl derivatives required 5·5 and 6·7 c.c. of *N*-sodium hydroxide respectively (theoretical, 9·2 c.c.), whilst 1 gram of the *iso*butyl derivative required 7·2 c.c. (theoretical, 8·5 c.c.).

Ethoxyacetamide, $EtO{\cdot}CH_2{\cdot}CO{\cdot}NH_2$.

This has been prepared by Sommelet (*Ann. Chim. Phys.*, 1908, [viii], **9**, 493) from the corresponding ester. The same substance was obtained by the reaction of ethoxyacetyl chloride and ammonia in dry ether. It crystallises from benzene in long needles, melting at 80—82°.

2-Ethoxymethylquinoxaline, $C_6H_4<\begin{matrix}N:C{\cdot}CH_2{\cdot}OEt\\ N:CH\end{matrix}$.

13·2 Grams (1 mol.) of α-oximino-γ-ethoxyacetone were mixed with 10·8 grams (1 mol.) of *o*-phenylenediamine and 12 grams (2 mols.) of glacial acetic acid diluted with 200 c.c. of water. The mixture was warmed on the steam-bath until a clear solution was obtained, and, after cooling, this was made alkaline with potassium hydroxide and distilled in a current of steam. The distillate was saturated with ammonium sulphate, and the quinoxaline extracted with ether. After drying and evaporating the ether, a bright yellow oil remained, which distilled at 237°/760 mm. and 144°/18 mm., yielding a pale yellow liquid. The quinoxaline has a faint, basic odour, becomes darker in colour on keeping, and is completely miscible with water, the solution reacting neutral towards litmus:

0·2262 gave 0·5786 CO_2 and 0·1159 H_2O. C = 69·38; H = 5·70.
0·2266 „ 29·3 c.c. N_2 at 18° and 738 mm. N = 14·45.
$C_{11}H_{12}ON_2$ requires C = 70·20; H = 6·38; N = 14·89 per cent.

On acidifying a solution of the base in water with hydrochloric acid, and evaporating to obtain the crystalline salt, decomposition ensued, and the concentrated solution acquired a deep blue colour. This made the preparation of the platinum salt difficult, and it could only be obtained in the following way.

One gram of the base was dissolved in 15 c.c. of ethyl alcohol (95 per cent.), and treated with 8 c.c. of a 10 per cent. alcoholic solution of platinum chloride. The *platinichloride* was immediately precipitated as a fine, yellow, crystalline powder, which was collected at once, washed with alcohol, and dried for a short time at 80°. It did not melt at 240°, but decomposed at 250°:

0·1621 gave 0·0388 Pt. Pt = 23·95.
$(C_{11}H_{12}ON_2)_2,H_2PtCl_6$ requires Pt = 24·52 per cent.

The *picrate* was obtained by treating a solution of the base in ethyl acetate with a solution of picric acid in the same solvent. It crystallises from methyl alcohol as a yellow powder, melting at 216°.

Pyrazine-2 : 5 : 6-*tricarboxylic Acid*, $\begin{matrix} CO_2H\cdot C\cdot N{:}C\cdot CO_2H \\ \| \qquad\quad | \\ CO_2H\cdot C\cdot N{:}CH \end{matrix}$.

Five grams of 2-ethoxymethylquinoxaline were dissolved in 500 c.c. of water and 35 c.c. of *N*-potassium hydroxide solution added. This solution was oxidised by the gradual addition of 32·5 grams of potassium permanganate dissolved in 1½ litres of water, the mixture being warmed on the steam-bath during the process. When the oxidation, which required about two hours, was complete, the cold solution was filtered from manganese dioxide, and the filtrate evaporated to 200 c.c. After acidifying with acetic acid, an excess of barium chloride solution was added, the liquid being heated to boiling during the addition. The precipitated barium salt was filtered, washed several times with hot water, suspended in cold water, and decomposed with about the necessary quantity of *N*-sulphuric acid. The barium sulphate was removed, the filtrate neutralised with ammonia, and a concentrated solution of calcium chloride added. The calcium salt of the acid remained in solution, and some calcium oxalate, which was precipitated, was removed by filtration. The filtrate was treated with barium chloride, and the precipitated barium salt was washed with hot water and digested with dilute sulphuric acid. After removing the barium sulphate, the solution was slowly evaporated in a desiccator until the acid crystallised. It was recrystallised from hot water and obtained in silky needles, which melted and decomposed at 191°:

0·4422 gave 0·6359 CO_2 and 0·0748 H_2O. C = 39·22; H = 1·88.
0·1358 ,, 16·05 c.c. N_2 at 17° and 761 mm. N = 12·91.
$C_7H_4O_6N_2$ requires C = 39·98; H = 1·88; N = 13·21 per cent.

The *copper* salt was obtained as a green, crystalline powder by the addition of a solution of copper nitrate to an aqueous solution of the acid. It was crystallised from water containing a little methyl alcohol:

0·1764 gave 0·0700 CuO. Cu = 31·69.
$C_{14}H_6O_{12}N_4Cu_3$ requires Cu = 31·30 per cent.

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MANCHESTER.

[*Received, April 15th*, 1915.]

LXXXVI.—*The Rotation of* iso*Butyl Diacetyl*-d-*tartrate.*

By Thomas Stewart Patterson and Donald Neil McArthur.

Some time ago we planned an investigation which, however, owing to the entry of one of us on other duties, had to be abandoned after the preparation of one of the compounds which we had proposed to examine. As it may not be possible to resume the research for some time, we desire to place on record the results so far obtained, as they may be useful in other connexions.

*iso*Butyl diacetyl-*d*-tartrate, prepared from *iso*butyl *d*-tartrate and acetyl chloride, is a liquid boiling at 183°/11 mm. Its rotation was examined at a number of different temperatures, with the following results:

$t°$	15·3	36·8	65·5	80·3	93·6
d	1·0899	1·0692	1·0420	1·0288	1·0168
α^t_D (100 mm.)	+17·31°	16·27°	15·53°	15·39°	15·33°
$[\alpha]^t_D$	+15·9	15·22	14·91	14·96	15·08
$[M]^t_D$	+55·01	52·66	51·59	51·77	52·17

$t°$	103·3	131	144·5	160	179
d	1·0080	0·9834	0·9720	0·9590	0·9430
α^t_D (100 mm.)	15·40°	15·72°	15·83°	15·95°	16·47°
$[\alpha]^t_D$	15·29	15·99	15·92	16·63	17·52
$[M]^t_D$	52·89	55·34	55·09	57·54	60·61

It will be observed that as the temperature rises, the rotation of the ester diminishes gradually, to reach a minimum value of $[M]_D$ +51·57° at 70°, thus showing a close resemblance to ethyl ditrichloroacetyltartrate and *iso*butyl ditrichloroacetyltartrate, which exhibit minima at +66° at 54°, and +88° at 105° (T., 1912, **101**, 378; 1913, **103**, 152).

The rotation of *iso*butyl diacetyl-*d*-tartrate was then determined in nitrobenzene solution of strength $p=9·6$. The data obtained were the following:

$p=9·68$.

$t°$	−4·2	+0·8	18·3	36·2	54·6	80·1
d	1·2148	1·2100	1·1926	1·1750	1·1568	1·1319
α^t_D (100 mm.)	−0·2°	−0·16°	−0·04°	+0·107°	0·253°	0·453°
$[\alpha]^t_D$	−1·7	−1·37	−0·35	+0·94	2·26	4·14
$[M]^t_D$	−5·88	−4·73	−1·20	+3·24	7·83	14·3

$t°$	93·2	110	117·5	125	141
d	1·1190	1·1028	1·0954	1·0888	1·0730
α^t_D (100 mm.)	0·52°	0·68°	0·733°	0·787°	0·907°
$[\alpha]^t_D$	4·80	6·37	6·92	7·46	8·73
$[M]^t_D$	16·61	22·04	23·93	25·8	30·21

It will be noticed that the rotation is greatly diminished on solution in this solvent, and that the temperature-rotation curve

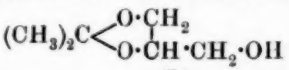
rises gradually as the temperature increases in such a way that the solution would be inactive at 24·5°. It may be concluded from the curvature of the graph that the minimum which was apparent in the graph for the homogeneous ester seems to have been shifted, by virtue of solution, towards a lower temperature and also towards a lower rotation value, thus again corresponding closely with the behaviour of the trichloroacetyl derivatives referred to above.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW. [*Received, May 6th*, 1915.]

LXXXVII.—*The Structure of Methyleneglycerol and Cinnamylideneglycerol. (Preliminary Note.)*

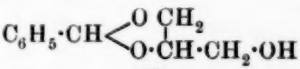
By DAVID HENRY PEACOCK.

IN a recent paper, Irvine, Macdonald and Soutar (T., 1915, **107**, 337) have shown that *iso*propylideneglycerol and benzylideneglycerol have the constitutions



(I.)

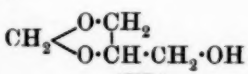
and



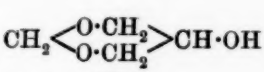
(II.)

The author has been for some time engaged in the investigation of the condensation products of glycerol with aldehydes and ketones, and in the course of this work has given particular attention to the structures of methyleneglycerol and cinnamylideneglycerol. Owing to the pressure of other work, this investigation is at present far from complete, but in view of the paper by Irvine and his collaborators, the following preliminary account is published.

Methyleneglycerol may have either of the constitutions III or IV:



(III.)



(IV.)

It will be apparent that a substance having constitution III contains an asymmetric carbon atom, and therefore the attempt has been made to resolve methyleneglycerol by the well-known hydrogen phthalate method of Pickard and Kenyon (T., 1911, **99**, 45). Methyleneglycerol is especially suitable for this, and was chosen from several of these condensation products because it is

much less readily hydrolysed than the others. The hydrogen phthalate was isolated, and from it the *brucine* salt was prepared:

0·1559 gave 5·81 c.c. N_2 at N.T.P. N = 4·6.

$C_{35}H_{38}O_{10}N_2$ requires N = 4·3 per cent.

On crystallisation from acetone, three fractions were obtained. 0·2 Gram of the first and second crops was made up to 25 c.c. with acetone, and the rotations in 2-dcm. tubes found to be −0·17° and −0·35°. There is thus evidence of resolution, indicating that formula III represents the constitution of methyleneglycerol. The work on the resolution of this acid ester is proceeding.

The aldehyde condensation products were prepared by a modified method, which it is hoped shortly to publish. In order to identify the compounds obtained, crystalline derivatives were sought. Methyleneglycerol gives with *o*-nitrobenzoyl chloride a well-defined *o-nitrobenzoate*, melting at 135°:

0·1470 gave 0·2818 CO_2 and 0·0609 H_2O. C = 52·28; H = 4·6.

$C_{11}H_{11}O_6N$ requires C = 52·17; H = 4·3 per cent.

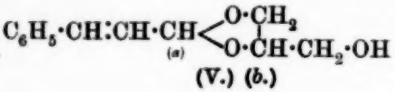
The other aldehyde condensation products were, however, usually hydrolysed on treatment with *o*-nitrobenzoyl chloride, and therefore recourse was had to phenylcarbimide as a means of producing crystalline compounds for identification. Methyleneglycerol gives the *phenylurethane*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_4O_2H_7$, melting at 129°:

0·1518 gave 0·3376 CO_2 and 0·0842 H_2O. C = 60·6; H = 6·1.

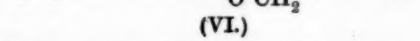
0·1867 „ 9·67 c.c. N_2 at N.T.P. N = 6·4.

$C_{11}H_{13}O_4N$ requires C = 59·2; H = 5·9; N = 6·2 per cent.

The structure of cinnamylideneglycerol is of much greater interest. This compound has not previously been described, but is readily obtained as a viscous oil, which slowly solidifies to a mass of crystals, melting at 110—112°. It is not so readily hydrolysed as benzylideneglycerol, but is less stable than the methylene compound. It may have either of the constitutions V and VI:



(V.)



(VI.)

In formula V the cinnamylidene group attached to the carbon atom (*a*), and the carbinol group attached to the carbon atom (*b*), may exhibit *cis-trans*-isomerism with respect to the heterocyclic ring. A similar possibility occurs in formula VI with respect to the cyclic structure there represented. In addition to this possi-

bility of isomerism, there is also that due to the double linking in the cinnamylidene group, which may again cause the formation of *cis*- and *trans*-isomerides. The number of possible isomerides for each formula is therefore four, neglecting optically active members.

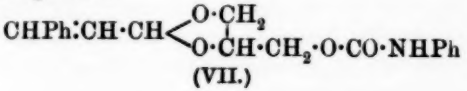
Cinnamylideneglycerol and phenylcarbimide, on heating until a vigorous reaction occurs, condense, and the product after crystallisation melts at 107°:

0·1170 gave 0·2975 CO_2 and 0·0623 H_2O. C = 69·3; H = 5·9.
0·1326 ,, 4·52 c.c. N_2 at N.T.P. N = 4·2.
$C_{19}H_{19}O_4N$ requires C = 70·1; H = 6·4; N = 4·3 per cent.

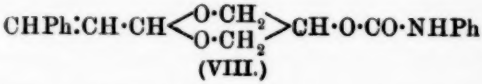
If, however, the components are heated at 150° for one hour, the product after crystallisation melts at 170°:

0·1480 gave 5·47 c.c. N_2 at N.T.P. N = 4·5.
$C_{19}H_{19}O_4N$ requires N = 4·3 per cent.

These are thus isomerides, and from a consideration of their modes of formation the isomerism is probably steric, and not structural, being due either to *cis-trans*-isomerism of the type exhibited by the hexahydrophthalic acids, or to isomerism, of the fumaric acid type, at the double linking. No further work has yet been done on these compounds, but their constitution may be decided on the following lines. On reduction, each will give the same dihydro-compound if the isomerism is due to the double linking, but not if it is due to the ring present. Again, the addition of hydrogen bromide at the double linking will develop enantiomorphism:



(VII.)



(VIII.)

If the compound has the structure VII, it already contains two asymmetric carbon atoms, and therefore the addition of hydrogen bromide will—unless a partial asymmetric synthesis occurs—give rise to two compounds, the *dd*, *ll* and *dl*,*ld* combinations. If the isomerism of these previously described phenylcarbamates is due to isomerism at the double linking in the cinnamylidene group, then, on the addition of hydrogen bromide, each should give the same two bromo-compounds, whilst if the isomerism is due to the ring it will persist, and each phenylcarbamate will, according to formula VII, give two distinct brominated compounds. If the carbamates have the constitution VII, then they possess no asym-

metric carbon atom, and the addition of hydrogen bromide to each, with the consequent formation of an asymmetric carbon atom, will give rise in each case only to one compound, the *dl* combination. If the original compounds owe their isomerism to spatial arrangement around the >C: C< linking, then the above compounds will be identical; whilst if the isomerism is of the hexahydrophthalic acid type, and due to the ring present, then the hydrogen bromide additive compound should still preserve this isomerism.

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ARDEER.

[*Received, April 28th*, 1915.]

LXXXVIII.—*Negative Colloidal Ferric Hydroxide.*

By FRANK POWIS.

IN studying the behaviour of suspension colloids, it is convenient to divide them into positive and negative, according to whether the particles move towards the cathode or anode, respectively, in an electric field. This movement shows there is a difference of potential between the particles and the medium in which they are suspended, and several suggestions have been made regarding the origin and sign of this.

Colloidal platinum and arsenious sulphide are usually regarded as typical negative colloids, and ferric hydroxide as a typical positive colloid. It has been known for some years, however, that in the presence of ferric chloride in greater concentration than about 0·3 millimol. per litre, the particles of colloidal platinum move towards the cathode like a positive colloid (Freundlich, "Kapillarchemie," p. 462). The explanation given for this was that the particles of platinum become coated with particles of positive colloidal ferric hydroxide formed by hydrolysis of the ferric chloride, and therefore the mixture behaves as a positive colloid. In a recent paper (*Zeitsch. physikal. Chem.*, 1914, **89**, 91) the present author has shown that aluminium chloride has a similar effect on the potential difference at the surface of particles of oil suspended in water, but has drawn the conclusion that this is due to the aluminium ions, and not to the hydroxide. The results obtained indicated that the cations of any electrolyte added to the water tend to make the potential difference less negative, and finally positive, and the anions to make it more negative. It was shown that in each case the effect of the ion increases considerably

with its valency, this being the reason why the potential difference becomes positive in the presence of a little aluminium chloride. According to these conclusions, it should be possible to convert any negative colloid into a positive one by the addition of a suitable electrolyte, that is, one where the effect of the cations greatly exceeds that of the anions; the case of platinum has been mentioned; arsenious sulphide and mercuric sulphide show a similar behaviour in the presence of suitable electrolytes (Freundlich, *Zeitsch. physikal. Chem.*, 1910, **73**, 385; Freundlich and Schucht, *ibid.*, 1913, **85**, 641), and the phenomena would appear to be quite general.

It therefore appeared interesting to determine whether, by the addition of an electrolyte the anions of which have a much more powerful effect than its cations, ferric hydroxide could be converted into a negative colloid. Suitable electrolytes would be those with a ter- or quadri-valent anion and univalent cation, and probably also alkali hydroxides, since these are known to act powerfully on positive colloids. With reference to this, a paper by Fischer (*Biochem. Zeitsch.*, 1910, **27**, 223) should first be mentioned. He added concentrated ferric chloride solution to sodium hydroxide solution containing glycerol, and thus obtained what he describes as negative colloidal ferric hydroxide. He does not appear to have made any cataphoretic determinations, his reason for saying it was negative being its solubility in the presence of sodium hydroxide. There is, moreover, some doubt as to the exact form in which the iron exists in the solutions containing glycerol, and therefore as to the relation of the product to ordinary positive colloidal ferric hydroxide. In the following, however, this is not so.

Colloidal ferric hydroxide was prepared by the addition of ammonium carbonate to ferric chloride solution and dialysis for several days, following the method used by Graham (Müller, "Chemie der Kolloide," p. 5), and was then considerably diluted. The resulting suspension had a conductivity of 7×10^{-5} mho at the ordinary temperature, showed the usual properties of colloidal ferric hydroxide, and therefore moved towards the cathode in an electric field. Sodium hydroxide was the electrolyte first chosen in the attempts to convert this into a negative colloid. On slowly adding a 5-millimolar solution, with constant shaking, quick coagulation of the ferric hydroxide took place when the concentration of the sodium hydroxide reached about 0·7 millimol. per litre. The author has shown (*Zeitsch. physikal. Chem.*, 1914, **89**, 186) that the coagulation of an oil emulsion takes place whenever the potential difference has a value below a certain limit, and has

cited evidence in favour of the view that this also holds in the coagulation of colloids. If this is so, in order to convert the ferric hydroxide into a negative colloid without coagulation taking place, the potential difference must change very quickly from a fairly high positive to a fairly high negative value. The best method of effecting this will be by adding the colloid to a sodium hydroxide solution which has a higher concentration than that which causes coagulation, rather than by quickly adding the hydroxide solution to the colloid; for in the former case the potential difference at the surface of each particle will be changed to a fairly high negative value immediately it enters the solution, and therefore before it has had time to stick to other particles; but in the second method, the concentration of the sodium hydroxide for a small interval will be such that the potential difference has a very low value, during which an appreciable amount of agglomeration may occur. Twenty c.c. of the colloid were therefore run from a pipette into 20 c.c. of 0·005*N*-sodium hydroxide solution, the flask being shaken during the whole time. A reddish-brown solution was obtained, which was quite clear, and showed no sign of precipitation either immediately or after keeping two days. The velocity of the particles in an electric field was determined by the method used by Burton (*Phil. Mag.*, 1906, [vi], **11**, 425), and found to be about 22 * towards the anode at 14°, corresponding with a potential difference of about −0·036 volt. (In all velocity measurements, the liquid in the upper half of the U-tube has had the same conductivity as that in the lower half, and contained the electrolyte or electrolytes calculated to be present in the latter. In calculating the potential difference, the dielectric constant has been taken as that for pure water.) After this negative colloid had been kept for two days, 15 c.c. were run from a pipette into 15 c.c. of freshly made 0·0075*N*-ferric chloride solution with constant shaking. The mixture was reddish-brown, quite clear, and again showed no sign of coagulation either immediately or after keeping for two days. The particles moved with a velocity of about 31 towards the cathode (temp. 14°), indicating a potential difference of approximately +0·050 volt. We must therefore conclude that the colloidal ferric hydroxide may be made either negative or positive at will, simply by suitable alteration of the electrolyte solution in which the particles are suspended. Since a very small concentration of ferric chloride will convert negative ferric hydroxide or platinum into positive colloids, as aluminium chloride changes the oil emulsion, it is not surprising that colloidal solutions of the hydroxides of the multivalent metals should

* Velocity in cm. $\times 10^{-5}$/sec. per volt/cm.

usually be found to be positive, because they are usually prepared either by dialysis of a solution of one of their salts (generally with a univalent anion), or by "dissolving" the hydroxide in a solution of one of the salts and then dialysing. In both cases the colloid is produced in the presence of a salt of a multivalent metal, and it is well known to be almost impossible to remove the whole of this by dialysis. It is therefore only to be expected that colloids produced under these conditions should be positive. By producing the particles in an electrolyte solution tending to give a negative potential difference, ferric hydroxide can, however, be easily obtained as a negative colloid without first preparing the positive form, as shown in the following experiment. One hundred c.c. of 0·01*N*-ferric chloride solution * were slowly run into 150 c.c. of 0·01*N*-sodium hydroxide solution, with constant shaking of the flask. A brownish-yellow solution (*A*) was obtained which was quite clear, and still showed no sign of coagulation after keeping in the stoppered flask for three weeks, although the addition of a little barium chloride to a sample caused immediate coagulation. In an electric field the particles moved towards the anode, the velocity corresponding with a potential difference of approximately −0·042 volt. Ferric hydroxide had therefore been produced as a negative colloid, there being no precipitation, although sodium hydroxide was present in excess, and all organic compounds were absent. On attempting to dialyse this solution against either distilled or conductivity water, coagulation took place in a few hours, the conductivity of the inside liquid having, in the meantime, considerably diminished. This is quite in accordance with the observations of previous investigators that a certain amount of electrolyte seems necessary for the stability of a colloidal solution, and may be explained in the manner indicated by the author (*loc. cit.*, p. 819), and supported by the observation of Freundlich and Schucht (*loc. cit.*) on the influence of hydrogen sulphide on colloidal mercuric sulphide. On running 20 c.c. of 0·01*N*-sodium hydroxide into 30 c.c. of 0·01*N*-ferric chloride so that the ferric hydroxide was produced and remained in the presence of ferric chloride, a yellowish-brown, stable, positive colloid (*B*) was obtained, the addition of sodium sulphate to some of this causing quick coagulation. If, however, equal quantities of the two 0·01*N*-solutions were mixed in either order, coagulation took place when nearly the whole of the second had been added, the flakes settling rapidly, and leaving the liquid above quite clear and

* Very dilute ferric chloride solutions are almost colourless when freshly prepared, but become brownish-yellow on keeping for a day (compare Wagner, *Kolloid Zeitsch.*, 1914, 14, 149); the solutions employed were therefore prepared only a short time before use by diluting a 0·4*N*-solution.

colourless. Similarly, on mixing equal volumes of the two colloidal solutions *A* and *B* in either order, coagulation occurred when nearly the whole of the second had been added.

In the last case, coagulation would usually be stated to be due to the negative particles in *A* attracting the positive ones in *B*, large groups thus being formed, which settle rapidly. It is known, however, that the potential difference at the surface of small particles changes very rapidly on adding an electrolyte (see, for instance, *Zeitsch. physikal. Chem.*, 1914, **89**, 179), that in a mixture of two oppositely charged colloids the particles all move in the same direction in an electric field, and that if one of them is in excess, and a little time is allowed while mixing, the order of mixing determines whether coagulation occurs or not. There is now also good evidence that the sign of the potential difference depends entirely on the character of the electrolyte solution in which the particles are suspended. In the author's opinion, these afford considerable evidence that changes in the potential difference occur more quickly than coagulation, the potential difference at the surface of the previously positive and negative particles becoming equal, or approximately equal, and its value then determining the stability of the mixture. This idea appears at first to be opposed to certain observations of the existence of both positive and negative particles in the same mixture, for example, by Kimura, and Godlewski (*Phil. Mag.*, 1914, [vi], **160**, 618). The author believes, however, that this is due to one or both of the substances being slightly soluble, and to the observations being made before sufficient time has elapsed for the solution to reach equilibrium, so that its composition is different in the immediate vicinity of the two kinds of particle. It might also be urged that the values obtained by the author (*loc. cit.*) for the potential difference at an oil–water and glass–water interface, with water as the medium, were not equal, being in the ratio of 1 to 1·7. The effect of adding various electrolytes was, however, almost the same in each case, and the concentrations at which each became zero were approximately the same; moreover, it must be remembered that the radius of curvature at the oil–water interface was only about 1 μ, whereas that at the glass–water interface was infinite, a fact which might have an appreciable influence on the value of the potential difference.

In support of the above observations on the production of positive and negative ferric hydroxide, it may be mentioned that Biltz (*Ber.*, 1904, **37**, 1095), by the addition of stannic chloride solution to an excess of ammonia solution, and subsequent dialysis, obtained stannic hydroxide as a negative colloid. On the other

hand, Glixelli (*Kolloid Zeitsch.*, 1913, **13**, 194), by hydrolysis of stannic chloride, obtained a gel of stannic hydroxide which behaved as positive, but on further washing, to remove the last traces of hydrochloric acid or stannic chloride, the potential difference passed through zero, and finally became negative.

In the author's opinion, the above results are most easily accounted for by assuming that ions are adsorbed on the surface of the colloidal particles from the electrolyte solution in which they are suspended, a view largely developed by Freundlich, although apparently now abandoned by him (see Elissafoff and Freundlich, *Zeitsch. physikal. Chem.*, 1912, **79**, 385). On this view, the ferric hydroxide is charged positively in the presence of a little ferric chloride, not because of the splitting off of hydroxyl ions, but because the ferric ions are so powerful in producing a positive potential that the effect of all the adsorbed cations exceeds that of all the anions. With a slight excess of sodium hydroxide, however, the hydroxyl ions are very effective, and almost all the ferric ions are removed, and so the potential difference is negative. The observation of Glixelli is very easily explained if, as agrees with many observations, the ions present in water of ordinary purity tend to give a negative potential difference.

It is usual to speak of a double layer of ions at the surface of colloidal particles, although it is doubtful how closely this represents the actual condition. It seems to be more probable that the concentration of each ion decreases gradually with increasing distance from the particle until it finally becomes equal to that in the bulk of the surrounding medium. This could easily be the case and yet there be an excess of anions in the layers nearest the particle, and of cations in those further away from it (or vice versa), so arranged that the total amounts present up to that distance where the concentration becomes equal to that in the bulk of the surrounding medium, are equivalent. With two electrolytes present, the author believes that the potential difference would be between those produced by each electrolyte separately (and not equal to their sum), except so far as the composition of the mixed solution does not represent the mean of those of the separate ones, owing to interaction or change in ionisation. Thus, whether the potential difference of a pure colloid is increased or decreased on adding an electrolyte will depend on whether its value in the presence of this electrolyte alone would be higher or lower than that due to the electrolyte present in the "pure" water —the view being taken that with the dialysed colloids usually employed the potential difference is due to traces of electrolyte

remaining, and that if these were removed its value would be zero. With a higher concentration of added electrolyte the effect of the ions originally present will become exceedingly small, and so the potential difference observed will be almost wholly due to the ions of the added electrolyte, and therefore its sign will depend on which of these is in excess in the layers nearest the particle, one tervalent ion, of course, being equal to three univalent ones.

Summary.

By adding colloidal ferric hydroxide to a dilute solution of sodium hydroxide of suitable concentration, it may be changed from positive to negative, coagulation being prevented by mixing in this order. It may also be directly prepared as a negative colloid by allowing the ferric hydroxide particles to form in the presence of a dilute solution of sodium hydroxide. The view is taken that the potential difference at the surface of colloidal particles is due to adsorption of ions from the solution, and that its sign depends on whether the cations or anions are in excess in the layers nearest the particles.

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[*Received, May 5th*, 1915.]

LXXXIX.—*A New Method of Finding the Second Dissociation Constants of Dibasic Acids.*

By ASWINI KUMAR DATTA and NILRATAN DHAR.

A MOLECULE of a dibasic acid, as is well known, generally dissociates in solution, yielding initially only one hydrogen ion. The second replaceable hydrogen atom does not appear as an ion until the first has for the most part assumed the ionic state. The first ionisation constant can always be determined by the electric conductivity method. The second dissociation constant is, however, very difficult to determine, and a trustworthy method has hitherto not been published, notwithstanding the researches of Noyes (*Zeitsch. physikal. Chem.*, 1893, **11**, 495), Trevor (*ibid.*, 1892, **10**, 321), Smith (*ibid.*, 1898, **25**, 144, 193), and Enklaar (*Chem. Weekblad.*, 1911, **8**, 824).

The method described in this paper is based on the fact that a solution of a normal salt of a strong base with a dibasic acid

dissolves more carbon dioxide than the same volume of water at the same temperature. In a solution of the salt hydrolysis occurs:

$$Na_2X + H_2O \rightleftarrows NaHX + NaOH.$$

When carbon dioxide is passed into the solution, hydroxidion combines with the hydrion of the carbonic acid, forming water, and at the same time hydrocarbanion (HCO_3') is formed:

$$NaOH + H_2CO_3 = NaHCO_3 + H_2O.$$

Moreover, the weak carbonic acid decomposes a small part of the salt according to the following reaction:

$$Na_2X + H_2CO_3 \longrightarrow NaHX + NaHCO_3.$$

Now, let a be the concentration of the carbon dioxide dissolved in a given volume of water. Carbonic acid is a very weak acid, and we may assume that it is not ionised at all. Let s be the concentration of the carbon dioxide dissolved in the same volume of a solution of a salt of concentration c. The concentration of the excess of carbon dioxide dissolved in the salt solution is, therefore, $s-a$. This is, as will be seen from what has been said above, also the concentration of the hydrocarbanion in the solution. The first dissociation constant of carbonic acid has been carefully determined by Walker (*Zeitsch. physikal. Chem.*, 1900, **32**, 137), the value being 3×10^{-7}. The concentration of the hydrogen ions in the solution is obtained from the following relation:

$$[H^\cdot][HCO_3']/[H_2CO_3] = 3 \times 10^{-7},$$

or

$$[H^\cdot] = a \,.\, 3 \times 10^{-7}/(s-a).$$

The concentration of the ion HX of the dibasic acid is, as will be seen from the reactions indicated above, equal to the concentration of the hydrocarbanion. Therefore, the concentration of the negative radicle of the salt $= c - 2(s-a)$. The second dissociation constant of the dibasic acid is therefore:

$$\frac{[H^\cdot][X']}{[HX]} = \frac{a \times 3 \times 10^{-7} \times \{c - 2(s-a)\}}{(s-a)^2} = K.$$

In the above calculation the salt is supposed to be totally dissociated, which is not the case; a correction for the ionisation of the salt is necessary. The corrected value of the dissociation constant K is obtained by allowing for this correction (Sand, *Zeitsch. physikal. Chem.*, 1904, **48**, 610; Bauer, *ibid.*, 1906, **56**, 250). The percentage of ionisation is calculated from the conductivity data given in Kohlrausch and Holborn's "Leitvermogen der Elektrolyte," Leipzig, 1898. Nernst suggested a similar method for the determination of the dissociation constant of monobasic acids, the general applicability of which was confirmed by Dhar and Datta (*Zeitsch. Elektrochem.*, 1913, **10**, 407; see also Dhar, *J. Amer. Chem. Soc.*, 1913, **35**, 800).

Experimental.

The appartus is an arrangement in series of a 250 c.c. Erlenmeyer flask, two U-tubes containing calcium chloride, a second flask as similar as possible to the first in shape and size, two U-tubes containing calcium chloride, and a guard-tube. The flasks each contain 100 c.c. of distilled water, and a weighed quantity of the salt is added to the first. The flasks are suitably closed, and are weighed with their contents. The U-tubes are filled with carbon dioxide, closed, and weighed. The apparatus is adjusted as described above, and carbon dioxide is slowly passed through it for about one hour until the contents of the flasks are saturated with the gas. The flasks and the U-tubes are again weighed, and the increase in weight of each flask and its two succeeding U-tubes is ascertained. The difference of these two increments is the measure of the weight of carbon dioxide dissolved in the salt solution in excess of that dissolved in the pure water in the second flask. From the increment in weight of the second flask the solubility of carbon dioxide in water under the given conditions is calculated. In some experiments carbon dioxide was passed again through the whole apparatus for about half an hour, and the flasks and tubes were re-weighed, but it was almost always found that the liquids were saturated in one hour. By the compensating arrangement described above a very small excess in solubility can be accurately determined, any error due to slight changes of temperature and pressure of the atmosphere being obviated. The Erlenmeyer flasks contain air when first weighed, and subsequently carbon dioxide. This difficulty is also removed by the compensating arrangement. The salts were almost always recrystallised before use. The mean temperature of the experiments was 25°. The figures in brackets in the last column of the table are Smith's values of $K \times 10^6$ at 100°.

Tartaric Acid (Rochelle salt).

Salt concentration	Ionised part Per cent.	Excess of Carbon dioxide dissolved.	Concentration of hydro-carbanion.	$10^6 \times K$.	Corrected $K \times 10^6$.
0·05535	71	0·0101	0·0023	99·3	70·5
0·05405	70	0·0099	0·00225	101·0	70·7
0·08600	68	0·0128	0·0029	98·7	67·1
				Mean.....	69·0 (58)

Succinic Acid (sodium salt).

Salt concentration	Ionised part Per cent.	Excess of Carbon dioxide dissolved.	Concentration of hydro-carbanion.	$10^6 \times K$.	Corrected $K \times 10^6$.
0·18154	60	0·0810	0·01840	4·5	2·7
0·09568	67	0·0577	0·01311	4·3	2·9
0·05860	70	0·0420	0·00955	4·7	3·2
			Mean.....		2·9 (2·3)

Malonic Acid (sodium salt).

0·04080	73	0·0460	0·01045	1·8	1·31
0·04660	71	0·0483	0·01100	2·0	1·42
0·04452	72	0·0473	0·01084	1·9	1·37
			Mean.....		1·36 (1)

Oxalic Acid (sodium salt).

0·02340	78	0·1003	0·00234	35·7	27·9
0·02043	80	0·0089	0·00202	41·6	33·2
0·01031	88	0·0062	0·00141	38·1	33·5
			Mean.....		31·0 (18)*

* Enklaar's value.

Fumaric Acid (sodium salt).

0·03560	75	0·0123	0·00280	36·3	26·5
0·03213	74	0·0119	0·00270	35·2	26·0
0·02604	77	0·0106	0·00241	36·8	28·3
			Mean.....		26·9 (18)

Malic Acid (sodium salt).

0·0718	69	0·0282	0·00641	14·0	9·66
0·1375	63	0·0420	0·00950	12·3	8·75
0·0895	68	0·0331	0·00752	12·8	8·70
			Mean.....		9·03 (8·3)

Phthalic Acid (sodium salt).

0·0405	73	0·0410	0·00932	2·5	1·84
0·0223	78	0·0282	0·00641	2·3	1·79
0·0622	70	0·0529	0·01202	2·6	1·82
			Mean.....		1·82 (1·7)

From the researches of Noyes and his pupils (*Zeitsch. physikal. Chem.*, 1903, **46**, 323) it is evident that the degree of dissociation of electrolytes generally decreases with increase of temperature. Our values are determined at 25°, so they are generally higher than those of Smith, which were measured at 100°.

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[*Received, January 12th*, 1915.]

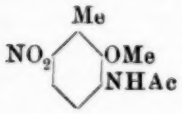
XC.—*The Nitration of 3-Acetylamino-2-methoxytoluene.**

By JOHN LIONEL SIMONSEN and MUDLAGIRI NAYAK.

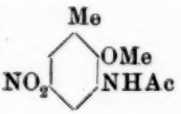
IN a recent communication (Cain and Simonsen, T., 1914, **105**, 156) the preparation of two of the three isomeric nitro-2:3-dimethoxybenzoic acids was described, namely, 5-nitro-2:3-dimethoxybenzoic acid and 6-nitro-2:3-dimethoxybenzoic acid. In view of the fact that neither of these acids was identical with the nitrodimethoxybenzoic acid obtained by the oxidation of nitrosantalin dimethyl ether (Cain and Simonsen, T., 1914, **105**, 340), it appeared of importance to attempt to devise a method for the synthesis of 4-nitro-2:3-dimethoxybenzoic acid. Further, in a recent communication, Perkin and Robinson (T., 1914, **105**, 2390) have synthesised 6-nitro-2:3-dimethoxybenzoic acid, and this investigation throws some doubt on the constitution of the acids previously described (Cain and Simonsen, *loc. cit.*).*

We have, therefore, carefully investigated the nitration of 3-*acetylamino*-2-*methoxytoluene*, since it appeared probable that this substance would lead to a synthesis of the nitro-acids by a method which would leave no doubt as to their constitution.

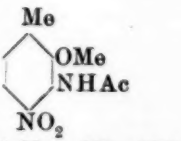
When 3-acetylamino-2-methoxytoluene was nitrated under the conditions described in the experimental part of this paper (see p. 830), the three isomeric nitroacetylaminomethoxytoluenes were formed. The separation of these three substances offered considerable difficulty, but ultimately a method was devised which gave satisfactory results.



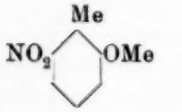
(I.) M. p. 119°.
Amine, m. p. 103°.



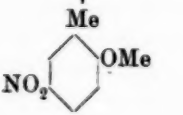
(II.) M. p. 141·2°.
Amine, m. p. 113°.



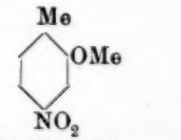
(III.) M. p. 170—171°.
Amine, m. p. 72°.



(IV.) M. p. 52°.



(V.) M. p. 62—63°.



(VI.) M. p. 73°.

* An abstract of this paper was read at the Second Indian Science Congress held in Madras on January 15th, 1915.

The main product of the nitration was found to be 6-*nitro*-3-*acetylamino*-2-*methoxytoluene* (I), m. p. 119°, whilst only traces of 4-*nitro*-3-*acetylamino*-2-*methoxytoluene* (III), m. p. 170—171°, were formed. The constitution of the acetyl derivative melting at 119° was readily proved in the following manner. On hydrolysis it yielded the amine melting at 103°, which, on reduction with tin and hydrochloric acid, gave a diamine showing all the properties of a para-diamine. Furthermore, on diazotisation it yielded a nitromethoxytoluene, melting at 52°, which was not identical with either 5-nitro-2-methoxytoluene (V), which melts at 62—63°, or 4-nitro-2-methoxytoluene (VI), melting at 73°. It must therefore be 6-*nitro*-2-*methoxytoluene* (IV), and hence the acetyl derivative of melting point 119° must be 6-*nitro*-3-*acetylamino*-2-*methoxytoluene* (I).

The second product of the nitration was an acetyl derivative melting at 141—142°, yielding on hydrolysis an amine melting at 113°. This was found to be 5-*nitro*-3-*amino*-2-*methoxytoluene* (II), since when the amino-group was eliminated it yielded 5-*nitro*-2-*methoxytoluene* (V), melting at 62—63°. This substance has not, so far as we are aware, been prepared, and we therefore obtained a specimen by the methylation of 5-nitro-*o*-cresol, and found it to be identical in every respect with the substance obtained from the nitroamine.

So far, 4-*nitro*-3-*amino*-2-*methoxytoluene* has only been isolated in a quantity insufficient for a detailed examination, but we hope to subject it to a careful investigation when more material is available. We next attempted to replace the amino-group in 6-nitro-3-amino-2-methoxytoluene and 5-nitro-3-amino-2-methoxytoluene by a hydroxy-group in order to prepare the corresponding nitrodimethoxytoluenes. In this we have, however, so far not been successful. Under all the conditions which we have employed, the sole product of the diazotisation has been the nitromethoxytoluene, the elimination of the amino-group having taken place. This result is somewhat remarkable, although van Hove (*Bull. Acad. roy. Belg.*, 1914, 235) describes experiments on the diazotisation of the phenetidines in which, in place of the catechol and quinol ethers, a yield of 43 per cent. of phenetole was obtained.

It is hoped that it may be possible later, when more material has been obtained, to devise a method for the preparation of the phenols, since it would enable us to orientate definitely the three nitro-2 : 3-dimethoxybenzoic acids.

Experimental.

*Nitration of 3-Acetylamino-2-methoxytoluene.**

As the result of numerous preliminary experiments, the following method was found to yield the most satisfactory results.

3-Acetylamino-2-methoxytoluene (10 grams) was finely powdered and added in small portions to fuming nitric acid (D 1·52) (20 grams) cooled in ice. The acetyl derivative gradually dissolved, and, after keeping for about fifteen minutes, the reaction mixture was poured on ice, when a yellow oil separated, which rapidly solidified. The yield varied somewhat, but it was found that the acetylamine (37 grams) gave approximately 48 grams of the mixed nitroacetylamines.

As was only to be expected, an examination of the nitration product showed it to be a mixture of the three isomeric nitroacetylamines, and it was only after a long series of experiments that the following somewhat laborious method of separation was devised.

In one experiment, the mixture of the nitroacetylamines (48 grams) was dissolved in hot alcohol (90 per cent.) (250 c.c.); after keeping the solution for some time, a considerable quantity (26 grams) of a crystalline solid separated in clusters of needles (*A*). These were collected, and the filtrate was evaporated to dryness on the water-bath, when a further quantity of a crystalline solid (*B*) was obtained.

The fraction *A* was recrystallised from boiling water (4 litres), when the greater portion dissolved. The sparingly soluble solid (*C*) was collected by filtering through a hot-water funnel, and the filtrate allowed to crystallise, when a solid separated in woolly needles (20 grams), melting at 95—97°. This was, at first, considered to be a pure substance, since, on further crystallisation, the melting point was not altered. However, it was found that the base which resulted on hydrolysis could readily be separated into two substances. For this purpose, the acetyl derivative, melting at 95—97° (20 grams), was hydrolysed by boiling with concentrated hydrochloric acid (60 c.c.) for three hours. On basifying, the amine separated as an oil, which rapidly solidified. This was collected and purified by crystallisation from methyl alcohol, when

* So far as we are aware 3-acetylamino-2-methoxytoluene does not appear to have been previously prepared. It was readily obtained by acetylating 3-amino-2-methoxytoluene with acetic anhydride and crystallises from hot water in needles melting at 100–101°:

0·1348 gave 0·3292 CO_2 and 0·0907 H_2O. C = 66·6; H = 7·4.
$C_{10}H_{13}O_2N$ requires C = 67·0; H = 7·3 per cent.

the base separated in highly characteristic, massive rhomboids, melting at 103°. This was found to be 6-*nitro*-3-*amino*-2-*methoxytoluene*.

The solution from which this substance had separated was evaporated to dryness, and the amine was reconverted into the acetyl derivative by boiling for a few minutes with acetic anhydride. The nitroacetylamine (12 grams) was recrystallised from hot water (1 litre), when a sparingly soluble portion remained undissolved. This was collected and added to the residue *C* (see above). The aqueous solution deposited a voluminous precipitate of woolly needles, melting at about 97°. These were collected and hydrolysed as described above, and the amine was crystallised from methyl alcohol, when a further quantity of pure 6-nitro-3-amino-2-methoxytoluene was obtained. This laborious process was then repeated until no further separation into a sparingly soluble acetyl derivative and a base melting at 103° could be effected.

The fraction *B* (20 grams) was hydrolysed by boiling with hydrochloric acid, and, on basifying, the nitroamine separated as an oil. This was dissolved in ether, the solution dried and evaporated, and the resulting oil kept for some days, when it partly solidified. After draining on porous porcelain, the solid was subjected to the above-mentioned process of purification.

The porous porcelain, which contained a considerable quantity of oil, was extracted with methyl alcohol, and the oily nitroamine was distilled in a current of steam from a weakly acidic solution. A base rapidly passed over and crystallised in orange-coloured needles, melting at 72°, and was evidently 4-*nitro*-3-*amino*-2-*methoxytoluene*.

The sparingly soluble nitroacetylamine (*C*) was purified by crystallisation from alcohol, when it separated in fine, iridescent needles, decomposing at 127°. This was identified as 5-*nitro*-3-*acetylamino*-2-*methoxytoluene*. The yield of pure nitroamines obtained from the acetylamine (37 grams) was 6-nitroamine (15 grams), 5-nitroamine (9 grams), and 4-nitroamine (1 gram).

6-*Nitro*-3-*amino*-2-*methoxytoluene* (I).—This nitroamine separated from methyl alcohol in massive, pale yellow rhomboids, melting at 103°:

0·1000 gave 0·1930 CO_2 and 0·0519 H_2O. C = 52·6; H = 5·7.

$C_8H_{10}O_3N_2$ requires C = 52·7; H = 5·5 per cent.

It is readily soluble in most organic solvents, but more sparingly so in cold methyl alcohol. It is a somewhat feeble base, and is readily extracted from an acid solution by ether. When reduced with tin and hydrochloric acid it yielded the *diamine*, which

separated on basification of the hydrochloride as a colourless solid, which, however, very rapidly became deep red, and could not be isolated in a pure state. It exhibited the usual properties of a para-diamine.

6-*Nitro*-3-*acetylamino*-2-*methoxytoluene*, prepared in the usual manner, separated from water containing a little alcohol in slender needles, melting at 119—120°. For analysis it was dried at 100°:

0·1107 gave 0·2173 CO_2 and 0·0550 H_2O. C = 53·5; H = 5·5.
$C_{10}H_{12}O_4N_2$ requires C = 53·6; H = 5·3 per cent.

Diazotisation of 6-*Nitro*-3-*amino*-2-*methoxytoluene*.

Numerous experiments were made under the most varied conditions with a view of converting the nitroamine into the phenol, but so far they have proved unsuccessful. In every case the sole product of the reaction that could be isolated was 6-*nitro*-2-*methoxytoluene*, the amino-group having been replaced by hydrogen.

In one experiment the amine (5 grams) was dissolved in an excess of dilute sulphuric acid, and the sparingly soluble sulphate diazotised with the calculated quantity of sodium nitrite. As soon as the diazotisation was complete, the solution of the diazonium sulphate was slowly added to a boiling 10 per cent. solution of sulphuric acid (250 c.c.). Nitrogen was only slowly evolved, and a considerable amount of tar separated. When the reaction was completed, the solution was extracted with ether, the ether filtered from undissolved tarry matter and evaporated, and the residual oil subjected to steam distillation. The oil which passed over rapidly solidified; the solid, after draining on porous porcelain, was recrystallised from dilute methyl alcohol, when it separated in needles, melting at 52—53°. It evidently consisted of 6-nitro-2-methoxytoluene (IV), a substance which, so far as we are aware, has not previously been prepared:

0·1127 gave 0·2393 CO_2 and 0·0570 H_2O. C = 57·9; H = 5·6.
$C_8H_9O_3N$ requires C = 57·5; H = 5·4 per cent.

The steam distillate from which this methyl ether had been separated was saturated with ammonium sulphate and extracted several times with ether, and the ether was dried and evaporated, when a small quantity of a solid was obtained, which crystallised from water in woolly needles, melting at about 147°, and probably consisted of 6-nitro-*o*-cresol, which is stated to melt at 143° (Ullmann, *Ber.*, 1884, **17**, 1961). When methylated with methyl sulphate in the usual manner it yielded a methyl ether, melting at 52—53°, identical with the substance described above.

The residue from the steam distillation, which consisted of a resinous, brown oil, evidently contained a quantity of this cresol, since on methylation it yielded more 6-nitro-2-methoxytoluene.

5-Nitro-3-acetylamino-2-methoxytoluene (II).

This *nitroacetylamine* was readily obtained as described above (see p. 831). It separated from alcohol in long, iridescent, prismatic needles, which decomposed at 127°, and contained one molecule of water of crystallisation. The anhydrous substance melted at 141—142°:

0·2988 dried at 100° lost 0·0211 H_2O. $H_2O=7·0$.

*0·1170 gave 0·2306 CO_2 and 0·0601 H_2O. $C=53·7$; $H=5·7$.

$C_{10}H_{12}O_4N_2$ requires $C=53·6$; $H=5·3$ per cent.

$C_{10}H_{12}O_4N_2,H_2O$ requires $H_2O=7·4$ per cent.

When 5-nitro-3-acetylamino-2-methoxytoluene was hydrolysed with concentrated hydrochloric acid, it gradually passed into solution, and the very sparingly soluble *hydrochloride* of the base separated. This was decomposed with potassium hydroxide, and the base was collected and purified by crystallisation from methyl alcohol:

0·1158 gave 0·2247 CO_2 and 0·0623 H_2O. $C=52·9$; $H=5·9$.

$C_8H_{10}O_3N_2$ requires $C=52·7$; $H=5·5$ per cent.

5-Nitro-3-amino-2-methoxytoluene (II) crystallises from methyl alcohol, in which it is somewhat readily soluble, in fine, sulphur-yellow needles, melting at 113°. It appeared to be a stronger base than the 6-nitroisomeride. When reduced with tin and hydrochloric acid it yielded the *diamine*, which was very unstable, and oxidised with extreme rapidity in the air. It exhibited all the usual properties of a meta-diamine.

Diazotisation of 5-Nitro-3-amino-2-methoxytoluene. 5-Nitro-2-methoxytoluene (V).

For the preparation of this substance, the nitroamine (0·5 gram) was dissolved in alcohol (10 c.c.), and, after the addition of sulphuric acid (0·5 gram), amyl nitrite (1 gram) was carefully added to the ice-cold solution. The sparingly soluble sulphate rapidly dissolved, and as soon as the diazotisation was completed, zinc dust (0·2 gram) was added, and the reaction mixture slowly heated to boiling. When all evolution of nitrogen had ceased, the solution was filtered from undissolved zinc and poured into water, when a solid separated. This was collected, freed from a little

* Dried at 100°.

red-coloured impurity by distillation in a current of steam, and crystallised from dilute methyl alcohol:

0·0938 gave 7·5 c.c. N_2 at 28° and 761 mm. N = 8·8.
$C_8H_9O_3N$ requires N = 8·4 per cent.

5-*Nitro*-2-*methoxytoluene* separates from methyl alcohol in colourless needles, melting at 63°.

For the purpose of comparison, a specimen of this substance was prepared by the methylation of 5-nitro-*o*-cresol, and was found to melt at 63°. No depression of melting point occurred on mixing these two substances:

0·1300 gave 0·2754 CO_2 and 0·0657 H_2O. C = 57·8; H = 5·7.
$C_8H_9O_3N$ requires C = 57·5; H = 5·4 per cent.

It may be mentioned that many attempts were made to convert the nitroamine into the corresponding cresol. Even when the pure diazonium salt was isolated and heated in aqueous solution, the sole product of the reaction that could be isolated was 5-nitro-2-methoxytoluene.

4-*Nitro*-3-*amino*-2-*methoxytoluene* (III).

This nitroamine was obtained in small quantity from the nitration product as described above (see p. 831), and has been only incompletely investigated. It crystallises from methyl alcohol in deep orange-coloured prismatic needles, melting at 72°:

0·1188 gave 0·2306 CO_2 and 0·0582 H_2O. C = 52·9; H = 5·4.
$C_8H_{10}O_3N_2$ requires C = 52·7; H = 5·5 per cent.

4-*Nitro*-3-*amino*-2-*methoxytoluene* is readily soluble in most organic solvents. It appears to be a weak base, and is somewhat readily volatile with steam.

Its *acetyl* derivative crystallises from hot water, in which it is much more readily soluble than its isomerides, in hexagonal prisms, melting at 170—171°.

THE PRESIDENCY COLLEGE,
MADRAS.

[*Received, April 26th,* 1915.]

XCI.—*The Constituents of* Gloriosa superba.

By Hubert William Bentley Clewer, Stanley Joseph Green and Frank Tutin.

The climbing, liliaceous plant, *Gloriosa superba*, Linn., occurs throughout India and Ceylon, and is there common on hedges during the rainy season. It is known by a large number of vernacular names, and in English as the "Superb Lily." The flowers are used by the Hindus in the worship of Siva and the Lingam, whilst the roots, which form elongated tubers, are reputed to possess medicinal properties, and were included by the Sanskrit writers in the seven minor poisons of India (*Pharmacographia Indica*, 1893, III, 480). The tubers are stated to be used for a variety of medicinal purposes, but chiefly for promoting labour pains and procuring abortion.

The only examination of the drug in question which appears hitherto to have been made was conducted by Warden (*Ind. Med. Gaz.*, 1880, **15**, 253; 1881, **16**, 138), who states that the root contains a neutral, bitter principle, named "superbine," three resins, a fluorescent principle, and salicylic acid. "Superbine" was considered to be either identical with, or closely allied to, the bitter principle of squill, and as little as 0·0107 gram of it proved fatal to a full-grown cat. Single determinations of the carbon, hydrogen, and nitrogen content gave results indicating the formula $C_{52}H_{66}O_{17}N_2$, which, however, was put forward with reserve.

The present investigation has shown that the bitterness of *Gloriosa* tubers is due to the alkaloid, colchicine, which has hitherto been known to occur only in Colchicum. Among other compounds which have now been isolated from *Gloriosa*, *2-hydroxy-6-methoxybenzoic acid* may be mentioned, as this substance has not hitherto been known. A summary of the results obtained will be found at the end of this paper.

Experimental.

The material employed for this investigation consisted of the tubers of *Gloriosa superba*, Linn., which had been specially collected in Ceylon, through the kindness of Mr. T. Petch, of the Botanical Bardens, Paradeniya.

Ten grams of the dried and ground material were digested with Prollius' fluid, and the resulting extract was tested with the usual alkaloid reagents, when reactions were obtained indicating the presence of a considerable amount of alkaloid.

In order to ascertain if an enzyme were present, 400 grams of the dried and ground tubers were macerated with water for eighteen hours, after which the liquid was expressed from the marc, and filtered. The filtrate was then treated with about twice its volume of alcohol, and the resulting brownish precipitate collected. When dry, the latter amounted to 4·3 grams. It contained a considerable proportion of inorganic matter, but had marked enzymic activity, since it readily hydrolysed amygdalin.

Twenty-five grams of the ground material were extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·135 gram	= 0·54	per cent.
Ether	,,	0·24 ,,	= 0·96	,, ,,
Chloroform	,,	0·11 ,,	= 0·44	,, ,,
Ethyl acetate	,,	1·02 ,,	= 4·08	,, ,,
Alcohol	,,	1·03 ,,	= 4·12	,, ,,
Total		2·535 grams	= 10·14	per cent.

For the purpose of a complete examination, 42·52 kilograms of the dried and ground tubers were thoroughly extracted by percolation with hot alcohol. After removal of the greater part of the alcohol, 10·35 kilograms of a dark brown extract were obtained. The whole of this extract was mixed with water and subjected to distillation in a current of steam, when 3·8 grams of a pale-coloured essential oil were obtained. This essential oil gave a colour reaction indicating the presence of furfuraldehyde, and distilled at 150—250°/15 mm. On keeping, it darkened in colour, and deposited some colourless crystals. The latter melted at 60°, and appeared to consist essentially of palmitic acid.

After the distillation of the extract with steam there remained in the distillation flask a dark brown, aqueous liquid (*A*), together with a quantity of dark-coloured resinous material (*B*). The latter was separated by filtration and well washed with hot water, the concentrated washings being added to the main bulk of the aqueous liquid.

Examination of the Aqueous Liquid (A).—The total quantity of the aqueous liquid, after being concentrated somewhat under diminished pressure, was extracted many times with ether, until the ethereal extracts were found no longer to contain alkaloid. The combined ethereal extracts were then concentrated, and completely extracted successively with aqueous hydrochloric acid, ammonium carbonate, sodium carbonate, and potassium hydroxide.

Isolation of an Alkaloid.—The acid extracts were rendered alkaline by means of sodium carbonate, and thoroughly extracted with ether, after which the ethereal extracts were concentrated

somewhat, and deprived of some phenolic material by means of aqueous potassium hydroxide. On evaporating the dried ethereal liquid, a residue was obtained, which slowly crystallised. The solid so obtained crystallised from ethyl acetate in small, very pale yellow leaflets, melting constantly at 177—178°, which were anhydrous. A further small amount of this base was obtained from the petroleum extract of the resin, as subsequently mentioned, the total amount isolated being about 0·75 gram:

0·1014 gave 0·2429 CO_2 and 0·0591 H_2O. C = 65·3; H = 6·5.
0·0890 „ 0·2141 CO_2 „ 0·0540 H_2O. C = 65·6; H = 6·7.
0·2776 „ 12·3 c.c. N_2 (moist) at 19° and 768 mm. N = 5·2.
0·1198 „ 0·2816 AgI. MeO = 31·0.

$C_{33}H_{38}O_9N_2$ requires C = 65·4; H = 6·3; N = 4·8; 6MeO = 31·7 per cent.

$C_{15}H_{17}O_4N$ requires C = 65·4; H = 6·3; N = 5·1; 3MeO = 33·8 per cent.

The results of the analyses given above agree best with the higher formula, but, owing to the small amount of material available, the possibility of the lower formula being the correct one could not be excluded. No gold salt could be obtained from this base, since it readily reduced auric chloride to the metallic state.

Isolation of Salicylic, 2-Hydroxy-6-methoxybenzoic and Benzoic Acids.—The ammonium carbonate extracts of the ethereal extract of the aqueous liquid were acidified, and extracted with ether. The crystalline residue obtained on evaporating the ether was dissolved in methyl alcohol, some sulphuric acid added, and the mixture heated for some time, after which the resulting ester was isolated. Although this process of esterification was repeated several times, the greater portion of the acid remained in the free state. The ester which was obtained, after being deprived of free acid, was separated into phenolic and non-phenolic portions by means of aqueous sodium hydroxide. The non-phenolic ester, which had the odour of methyl benzoate, yielded, on hydrolysis, a small amount of an acid, which crystallised from water in colourless leaflets, melting at 121°, and was identified as benzoic acid.

The phenolic ester, when hydrolysed, gave a mixture of acids which was found to be similar to the portion of the original acid mixture which had resisted esterification. The total quantity was therefore fractionally crystallised many times from a mixture of chloroform and benzene, when it was eventually separated into two compounds, melting at 155° and 135° respectively. The former of these products, which was the smaller in amount, proved to be salicyclic acid. (Found, C = 60·7; H = 4·5. Calc., C = 60·9; H = 4·4 per cent.)

The acid melting at 135° was similar in appearance to salicylic acid, and yielded the same colour with ferric chloride. A mixture of it with the latter acid, however, melted at about 120°:

0·1018 gave 0·2132 CO_2 and 0·0446 H_2O. C = 57·1; H = 4·8.

0·2393 „ 0·3269 AgI. MeO = 18·2.

$C_8H_8O_4$ requires C = 57·1; H = 4·8; MeO = 18·4 per cent.

It thus appeared that the acid melting at 135° was a methoxysalicylic acid. The only known acid of this character with which the compound from *Gloriosa* agrees at all in its properties is 2-hydroxy-5-methoxybenzoic acid, which melts at 141°. A quantity of the latter was therefore prepared from quinol monomethyl ether by Körner and Bertoni's method (*Ann. di chim. medicin*, 1881, 65), when the synthetic acid was found to differ from the naturally occurring one. Thus, a mixture of the two preparations melted at 118°, and the colour produced on treating the synthetic acid with ferric chloride was blue, whereas the natural acid yielded a violet colour identical with that furnished by salicylic acid. It therefore appeared that the acid melting at 135° occurring in *Gloriosa* must be *2-hydroxy-6-methoxybenzoic acid*, a compound which has not hitherto been known.

In order to confirm this assumption, resorcinol was heated at 120—130° with water and ammonium carbonate, when a mixture of 2 : 6- and 2 : 4-dihydroxybenzoic acids resulted (Senhoffer and Brunner, *Wien. Akad.*, 1879, 80). This crude mixture was then vigorously methylated by means of methyl sulphate and potassium hydroxide, and the product was heated for some time in alcoholic solution with an excess of the alkali. Water was then added, and the mixture extracted with ether, when a quantity of a crude ester which had resisted hydrolysis by the alkali was obtained. This product was distilled under the ordinary pressure, when the portion of higher boiling point solidified on cooling. On crystallising this product from petroleum, long, colourless needles, melting at 88°, were obtained. This compound must be *methyl 2 : 6-dimethoxybenzoate*, a substance not hitherto known, the fact of its not being hydrolysed by alcoholic potassium hydroxide being evidently due to steric hindrance caused by the two methoxy-groups in the ortho-position with respect to the carboxyl group. An identical ester was obtained by the methylation of the 2-hydroxy-6-methoxybenzoic acid occurring in *Gloriosa*:

0·1169 gave 0·2619 CO_2 and 0·0657 H_2O. C = 61·1; H = 6·2.

$C_{10}H_{12}O_4$ requires C = 61·2; H = 6·1 per cent.

The materials removed from the original ethereal extract of the aqueous liquid by the extractions with sodium carbonate and

potassium hydroxide previously mentioned were small in amount, and amorphous. After the extraction with these alkalis, the ether only contained a small amount of indefinite, fatty matter.

A portion of the original aqueous liquid (*A*) which had been extracted with ether, as previously described, was extracted many times with amyl alcohol, but it was found that the product so removed was chiefly of an alkaloidal nature, and was slowly extracted from the amyl alcohol by means of aqueous hydrochloric acid. The portion of the amyl alcohol extract which was not basic was small in amount, and amorphous. Nothing definite could be obtained from it by either acid or alkaline hydrolysis. It was subsequently found that the alkaloid remaining in the aqueous liquid after extraction with ether could be more conveniently removed by means of chloroform, and this method was therefore resorted to.

Isolation of Colchicine, $C_{22}H_{25}O_6N$.—The chloroform extract of the aqueous liquid gave a crystalline substance containing chloroform of crystallisation. When deprived of the solvent, the substance was amorphous. It could not conveniently be recrystallised from chloroform owing to its great solubility, but was eventually obtained crystalline from ethyl acetate. The product so obtained was then readily recrystallised from the last-mentioned solvent when dry, when it formed aggregates of small, soft needles, having a very pale yellow colour, and melting at 155—157°:

0·5813 * on drying in a vacuum lost 0·0086 H_2O. $H_2O = 1·5$.
0·1008 † gave 0·2428 CO_2 and 0·0620 H_2O. $C = 65·7$; $H = 6·8$.
0·3024 † „ 9·7 c.c. N_2 (moist) at 19° and 772 mm. $N = 3·7$.
0·1967 † „ 0·4561 AgI. $MeO = 30·6$.

$C_{22}H_{25}O_6N$ requires $C = 66·2$; $H = 6·3$; $N = 3·5$; $4OMe = 31·1$ per cent.

The properties and composition of this alkaloid suggested that it was colchicine, and, apart from the differences mentioned below, it was found to yield the reactions characteristic of the latter, as described in the United States Pharmacopœia. The colchicine, however, which is obtained from the corm or seeds of *Colchicum autumnale*, Linn., is described as an amorphous powder, melting at 142°, and has only been obtained crystalline in the form of a chloroform compound, containing three molecules of chloroform of crystallisation. For the sake of comparison, therefore, colchicine isolated from *Colchicum autumnale* was also investigated, and found to crystallise from ethyl acetate in soft, pale yellow needles, melting at 155—157°, alone or when mixed with the base derived from *Gloriosa superba*. With the object of further confirming the

* Air-dried. † Dried in a vacuum.

identity of the two preparations, their specific rotatory powers were compared with the following results:

0·1759* of the base from *Gloriosa*, made up to 20 c.c. with chloroform, gave α_D −2°8′ in a 2-dcm. tube, whence $[\alpha]_D^{16·5}$ −121·3°.

0·1759* of the base from *Colchicum*, made up to 20 c.c. with chloroform, gave α_D 2°7′ in a 2-dcm. tube, whence $[\alpha]_D^{16·5}$ −120·3°.

In both these determinations, and also in several others carried out in chloroform solution, it was noticed that the observed rotation dropped from 5—8′ during the first thirty minutes after solution, when it remained constant. The rotation of colchicine was also observed to vary very appreciably with the concentration, the specific rotation being less in more concentrated solutions when employing chloroform. A determination in aqueous solution yielded the following results:

0·3543,* made up to 20 c.c. with water, gave α −15°12′ in a 2-dcm. tube, whence $[\alpha]_D$ −429·0°.

The colchicine from *Gloriosa* yielded an aurichloride, which formed soft, yellow needles, and melted at 209° after drying over sulphuric acid:

0·0800 gave 0·0214 Au. Au = 26·7.

$C_{22}H_{25}O_6N,HAuCl_4$ requires Au = 26·7 per cent.

The above-recorded analysis of the colchicine seems to indicate that the latter still retained a small amount of water of crystallisation after drying in a vacuum, and this is probably the case, since the water which was lost was very rapidly reabsorbed on exposure to the air. On drying colchicine at 105°, however, some slight decomposition appeared to occur.

The amount of colchicine isolated in the pure state from *Gloriosa* was 16·5 grams, which is equivalent to approximately 0·04 per cent. of the weight of the drug employed. When, however, the dried and ground *Gloriosa* tubers were assayed for colchicine by the method described in the United States Pharmacopœia, the amount of alkaloid found was equivalent to 0·3 per cent. of the weight of the dried tubers.

A portion of the aqueous liquid (*A*) which had been extracted with ether and amyl alcohol was treated with a slight excess of basic lead acetate. A voluminous, yellow precipitate was thus produced, which was collected, washed, suspended in water, and decomposed by means of hydrogen sulphide. After the removal of

* Air-dried.

the lead sulphide, the filtrate was evaporated under diminished pressure. The product so obtained was dark brown, and amorphous. Nothing crystalline could be separated from it, and it gave only amorphous products when hydrolysed by means of acids or alkalis.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the lead, and the filtered liquid concentrated under diminished pressure to the consistency of a syrup. The latter evidently contained a considerable amount of dextrose, since it readily yielded *d*-phenylglucosazone (m. p. 217°), and, on acetylation, yielded β-pentaacetyldextrose (m. p. 130—131°). (Found, C = 49·3; H = 5·8. Calc., C = 49·2; H = 5·6 per cent.)

Isolation of Choline, $C_5H_{15}O_2N$.—A quantity of the original, aqueous liquid (*A*) which had been extracted with ether and chloroform was concentrated. The resulting syrupy liquid was extracted with alcohol, the alcoholic liquid evaporated, and the residue again treated with alcohol, this operation being repeated until a product was obtained which was soluble in nearly absolute alcohol. To the alcoholic liquid so obtained, a saturated alcoholic solution of mercuric chloride was added, and the mixture kept for several days. The precipitate which had formed was collected, washed with a little alcohol, dissolved as completely as possible in warm water, and the mercury removed from the filtrate by hydrogen sulphide. To the filtered, aqueous liquid, slightly acidified with sulphuric acid, a solution of phosphotungstic acid was added, the precipitate thus produced being treated with barium hydroxide, the mixture filtered, and the excess of barium removed by carbon dioxide. The clear solution was then neutralised with hydrochloric acid and evaporated, first under diminished pressure and finally in a vacuum desiccator, to dryness. The residue was extracted with cold, absolute alcohol, the solution decolorised by means of animal charcoal, and the filtered liquid evaporated. The residue was dissolved in a little water and treated with auric chloride, when a pale yellow precipitate was produced. The latter was collected and dried, when it proved to be choline aurichloride. (Found, Au = 44·3. Calc., Au = 44·5 per cent.) The amount of choline present in *Gloriosa* is, however, extremely small. Attempts to isolate asparagine from the aqueous liquid yielded a negative result.

Examination of the Resin (B).—The resin (*B*) was a hard, dark brown mass, and amounted to 436·4 grams, being thus equivalent to nearly 1·03 per cent. of the weight of the dried tubers employed. It was dissolved in alcohol, mixed with purified sawdust, and the

thoroughly dried mixture extracted successively, in a large Soxhlet apparatus, with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.—The petroleum extract of the resin amounted to 194·7 grams. It was dissolved in ether, and the ethereal solution shaken with 10 per cent. aqueous hydrochloric acid, which rapidly removed some alkaloidal material. The acid extracts were rendered alkaline by means of sodium carbonate, and extracted with ether, when the alkaloid was removed. On evaporating the ether, a small, dark-coloured residue was obtained, which slowly crystallised. This solid, when purified by crystallisation from ethyl acetate, yielded about 0·15 gram of the previously described alkaloid, $C_{33}H_{38}O_9N_2$, melting at 178°.

The ethereal solution which had been extracted with acid was then shaken with 30 per cent. aqueous potassium hydroxide, which removed the more strongly acid constituents, whilst the salts of the fatty acids remained in the ether. On acidifying the alkaline liquid so obtained and extracting it with ether, a product was obtained which was found to consist solely of benzoic, salicylic, and 2-hydroxy-6-methoxybenzoic acid. The original ethereal liquid was then washed with very dilute aqueous potassium hydroxide, when a dark-coloured, soapy liquid was obtained, the pale yellow, neutral constituents remaining dissolved in the ether. The alkaline liquid was then acidified, and extracted with ether, when a small amount of pale-coloured, flocculent solid remained undissolved. After removing the latter, the ethereal solution was again extracted with dilute, aqueous potassium hydroxide, when a further quantity of neutral material, which had been occluded during the first extraction with dilute alkali, remained dissolved in the ether. The final extract with dilute alkali was then acidified, and the acids extracted by means of ether, when an additional amount of the above-mentioned, flocculent solid was obtained.

Isolation of a Phytosterolin.—The above-mentioned sparingly soluble solid material which had been collected by filtration from the ethereal liquids, as above described, was heated with several successive portions of ethyl acetate to remove adhering fatty matter, after which it was extracted in a Soxhlet apparatus for several days with alcohol. A colourless, sparingly soluble substance was then slowly removed, which was collected, and recrystallised from dilute pyridine. It then formed colourless, microscopic crystals, which melted at 293°, and had the properties of a phytosterolin (phytosterol glucoside):

0·1339 gave 0·3548 CO_2 and 0·1260 H_2O. C = 72·3; H = 10·5.
$C_{33}H_{56}O_6$ requires C = 72·3; H = 10·2 per cent.

On heating the phytosterolin with acetic anhydride in the presence of pyridine, it yielded an acetyl derivative, which crystallised from alcohol in colourless leaflets, melting at 163°.

A quantity of the phytosterolin was hydrolysed by prolonged boiling with alcohol containing some hydrochloric acid, when it yielded a phytosterol. The latter, like the corresponding product occurring in the free state in the plant, described below, proved to be a mixture of stigmasterol and another alcohol, which was probably sitosterol. It is evident, therefore, that stigmasterol glucoside, and probably also sitosterol glucoside, occur in *Gloriosa*.

Examination of the Fatty Acids.—The ethereal solution of the fatty acids which had been separated by filtration from the crude phytosterolin, as above described, was evaporated, and the residual acids converted into their methyl esters by means of methyl alcohol and sulphuric acid. The resulting esters, together with the corresponding esters of the combined fatty acids, obtained as subsequently described, were purified by distillation under diminished pressure, when they passed over at 208—270°/15 mm. The purified esters were then hydrolysed, and the resulting acids separated into their saturated and unsaturated components by means of the lead salts in the usual manner. The saturated fatty acid, after purification by the distillation of its methyl ester, melted at 62°, and was found to consist of palmitic acid. (Found, C=75·0; H=12·5. Calc., C=75·0; H=12·5 per cent.)

The unsaturated fatty acids were small in amount, and distilled at 235—243°/15 mm. They gave C=76·7; H=11·7 per cent. Iodine value=127. A mixture of one part of linolic acid and two parts of oleic acid requires C=76·8; H=11·8 per cent. Iodine value=121.

The ethereal solutions of the neutral portions of the petroleum extract of the resin were evaporated, and the residue heated with an excess of alcoholic potassium hydroxide. The mixture was then diluted with water, and extracted many times with ether for the removal of the unsaponifiable material. The fatty acids were then isolated from the alkaline, aqueous liquid, and examined in connexion with the free fatty acids, as already described. The ethereal solution of the unsaponifiable material was evaporated, and the resulting pale yellow, crystalline residue crystallised from a considerable volume of absolute alcohol. The product thus obtained, which did not appear homogeneous, was recrystallised from alcohol until it no longer gave a reaction indicating the presence of phytosterol, when about 2·5 grams of a product of low melting point were obtained. Since the latter did not appear homogeneous, it was treated with phthalic anhydride in a manner previously

described (T., 1914, **105**, 1835), when it was ultimately separated into a fatty alcohol, melting at 77°, and a hydrocarbon, melting at 63—65°; both of these products, however, were insufficient for analysis.

Isolation of Stigmasterol.—The alcoholic mother liquors from the crude mixture of fatty alcohol and hydrocarbon were concentrated, and some ethyl acetate and a little water added. A considerable quantity of long, colourless plates then separated, which gave the colour reaction characteristic of the phytosterols. The entire product was heated with acetic anhydride, and the resulting acetyl derivative crystallised from alcohol until it melted constantly at 133°:

0·1007 gave 0·3003 CO_2 and 0·1020 H_2O. C = 81·3; H = 11·3.

0·2095, made up to 20 c.c. with chloroform, gave α_D −1·23° in a 2-dcm. tube, whence $[\alpha]_D$ −58·7°.

These results indicated the probability of this phytosterol being a mixture containing some stigmasterol. The above-described acetyl derivative was therefore treated with bromine in the manner described by Windaus and Hauth (*Ber.*, 1906, **39**, 4378; 1907, **40**, 3681), when a crystalline bromo-derivative rapidly separated. On recrystallising the latter from a mixture of chloroform and alcohol, small, glistening crystals, melting at 210°, were obtained, which were identified as tetrabromoacetylstigmasterol. When debrominated by means of zinc dust, the above compound yielded acetylstigmasterol (m. p. 140°), and the latter, on hydrolysis, was converted into stigmasterol, melting at 167°. The mother liquors from the crude tetrabromoacetylstigmasterol, when debrominated in a similar manner, and subsequently hydrolysed, yielded a small amount of a phytosterol, which, after recrystallisation, melted at 133°, and was probably sitosterol, but the amount obtained was not sufficient for its identity to be fully confirmed.

Ethereal Extract of the Resin.—The ethereal extract of the resin was dark brown, and amounted to 87·4 grams. It was digested with a litre of ether, when a portion of it, which remained undissolved, was removed by filtration. The ethereal solution was then shaken with 10 per cent. hydrochloric acid, when a quantity of an alkaloid was removed. The acid extracts were then rendered alkaline by means of sodium carbonate, and extracted, first with ether and subsequently with chloroform, since a portion of the alkaloid was only with great difficulty removed by the former solvent. On evaporating the chloroform extract, an amorphous, basic product was obtained, which will be referred to later, but the ethereal extracts, when evaporated to a moderately small volume, deposited a quantity (0·15 gram) of light, feathery needles.

The latter were collected, and recrystallised from ethyl acetate, when long, colourless needles, melting at 267°, were obtained:

0·0845 gave 0·2058 CO_2 and 0·0498 H_2O. C = 66·4; H = 6·7.

This substance contained nitrogen, and was a weak base, but the amount was too small to permit of the percentage of nitrogen being estimated. The percentage of carbon and hydrogen found, however, are in good agreement with those required for a methyl-colchicine, $C_{23}H_{27}O_6N$, namely, C = 66·8; H = 6·5 per cent.

The ethereal filtrate from the above-described crystalline base yielded, on evaporation, some amorphous alkaloidal material, which was added to the amorphous base obtained by extraction with chloroform mentioned above.

The original ethereal solution of the resin which had been extracted with acid, as above described, was thoroughly examined, when it was found to consist essentially of phenolic, resinous material, together with a minute quantity of a crystalline phenolic substance.

The above-mentioned portion of the ether extract of the resin which was not dissolved by digestion with ether was heated with chloroform, when a pale-coloured product remained undissolved. The latter, on examination, was found to consist of a further quantity of phytosterolin, identical with that previously described. The chloroform solution, when extracted with acid, yielded a further quantity of amorphous, basic product, but the remainder of the material contained in it was of a resinous nature.

The total amount of the various amorphous, basic products from the ether extract of the resin were united, dissolved in alcohol, and mixed with purified sawdust, and the thoroughly dried mixture was extracted in a Soxhlet apparatus for a long time with ether. The material thus removed was dissolved in chloroform, and deprived of some dark-coloured, phenolic material by means of aqueous potassium hydroxide. On then evaporating the dried chloroform solution almost to dryness, a residue was obtained which slowly crystallised. The latter was digested with ethyl acetate, and the solution filtered, when some brown, amorphous material, part of which was basic, was removed. On concentrating the ethyl acetate solution, a quantity of crystalline colchicine was obtained.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin was dark brown, and amounted to 87 grams. It yielded a further amount of colchicine, together with amorphous basic products. The portion of the

extract which was non-basic was thoroughly examined, but it yielded only resinous products, besides a small amount of the previously described 2-hydroxy-6-methoxybenzoic acid.

The ethyl acetate and alcohol extracts of the resin were dark brown, resinous masses, and amounted to 18·3 and 49 grams respectively. Nothing definite could be obtained from them, and they contained nothing of a glucosidic nature.

Summary and Physiological Tests.—The results of the foregoing investigation may be summarised as follows:

The material employed consisted of the dried tubers of *Gloriosa superba*, Linn., which had been specially collected in Ceylon. Preliminary tests showed the presence of an enzyme, which readily hydrolysed amygdalin, and a considerable amount of an alkaloid. An alcoholic extract of the ground material yielded, in addition to amorphous products, the following definite compounds: (1) Benzoic, *2-hydroxy-6-methoxybenzoic*, and salicylic acids; (2) choline; (3) dextrose; (4) palmitic and a mixture of unsaturated acids; (5) small amounts of a hydrocarbon (m. p. 63—65°) and a fatty alcohol (m. p. 77°); (6) a mixture of phytosterols which contained stigmasterol; (7) a mixture of phytosterolins, containing stigmasterol glucoside; (8) a mixture of alkaloids which consisted chiefly of colchicine, $C_{22}H_{25}O_6N$, together with small amounts of two other crystalline bases. The amount of colchicine present in the drug, when estimated according to the method of the United States Pharmacopœia, was found to be 0·3 per cent.

The physiological action of the colchicine from *Gloriosa* was compared with that of the base from *Colchicum autumnale* at the Wellcome Physiological Research Laboratories by Dr. J. H. Burn, to whom our thanks are due, when the two bases were found to be identical in their effects.

It is evident that the toxic properties of *Gloriosa* tubers are due, essentially, to the colchicine present.

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LONDON, E.C. [*Received, May 13th*, 1915.]